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RADIOCHEMICAL INVESTIGATION OF SPALLATION AND FISSION REACTION  
PRODUCTS RESULTING FROM THE BOMBARDMENT OF BISMUTH  
WITH 660-Mev PROTONS

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INTRODUCTION

A fairly detailed study has now been made of spallation reactions occurring as a result of the bombardment of light and medium-weight nuclei (e.g., Al [1], Fe [2], Cu [3, 4], As [5], Sb [6], Cs [7], Co [8], etc.) with high-speed particles. In all of these cases fission does not occur — at least not to a significant extent. When heavy elements are bombarded with high-speed particles, not only spallation reactions, but also fission reactions occur. The nature of these fission processes has been studied fairly thoroughly in an investigation [9] on the bombardment of bismuth with 190-Mev deuterons, but the products of the spallation reactions were not isolated. Spallation reactions (and also fission reactions) with 480-Mev protons were studied by us in collaboration with Nikitin [10], and also later by Bennett [11]; in the latter investigation only a few of the reaction products were studied and the absolute yields were not determined. In work on the bombardment of uranium with 380-Mev  $\alpha$ -particles [12], not only fission products, but also some spallation products were isolated, but again the latter were not studied in detail.

In the present work we have investigated spallation and fission reactions occurring when bismuth is bombarded with 660-Mev protons, and we have discovered some of the laws governing the process. We have estimated the ratio of the reaction cross-sections for fission and for spallation, and we have also made comparisons with results obtained for the bombardment of bismuth with protons of lower energy (480 Mev) and with results obtained by Perfilov and Ostroumov's method of thick-layer plates [13]. All these considerations enable us to form a fairly complete picture of the process that is occurring and to reach interesting conclusions.

EXPERIMENTAL

Chemical Separation of Reaction Products

The target was either a plate of pure bismuth, 3-6 mm in thickness, or pure bismuth oxide powder wrapped in aluminum foil. After the bombardment the target was brought into solution, and small amounts (10-20 mg) of inert carriers for elements to be isolated were added to the solution. Isolation of the radioactive elements with their carriers was then carried out.

We outline below the procedures employed for the isolation of radioactive fractions of individual elements in a radiochemically pure form. Nearly all of the operations indicated were repeated many times.

Fe. Extraction with ether from 6 N HCl; separation of TlI and sulfides insoluble in acid; precipitation of  $\text{Fe}(\text{OH})_3$  with excess of ammonia.

Cu. Separation of hydroxides insoluble in ammonia (together with iron), separation of AgCl; precipitation of CuCNS from acid solution after reduction with  $\text{SO}_2$ .

Sr. Separation of sulfides insoluble in acid, and also  $\text{Fe}(\text{OH})_3$ ; separation of Ca with a mixture of alcohol and ether from the dry nitrates; separation of  $\text{BaCrO}_4$ ; precipitation of  $\text{SrCO}_3$  and  $\text{SrSO}_4$ .

Mo. Extraction with ether from 6 N HCl after oxidation; separation of  $\text{Fe}(\text{OH})_3$  with ammonia; precipitation with  $\alpha$ -benzoinoxime from 3 N  $\text{HNO}_3$ , and then as  $\text{MoS}_3$ .

Ag. Precipitation of AgCl, dissolution in ammonia and separation of Fe(OH)<sub>3</sub>; precipitation of Ag<sub>2</sub>S in an ammoniacal medium; precipitation of AgCl.

Ba. Separation of sulfides insoluble in acid, and Fe(OH)<sub>3</sub> with ammonia; precipitation of BaCO<sub>3</sub>, BaCrO<sub>4</sub>.

Ce. Precipitation as CeF<sub>3</sub>; precipitation as Ce(IO<sub>3</sub>)<sub>3</sub> after oxidation with KBrO<sub>3</sub>; separation of Zr(IO<sub>3</sub>)<sub>4</sub> after reduction with hydrogen peroxide; precipitation of Ce(OH)<sub>3</sub> and Ce<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>.

W. Precipitation of tungstic acid, dissolution in ammonia, and separation of Fe(OH)<sub>3</sub>; separation of Ag<sub>2</sub>S in ammoniacal medium; separation of MoS<sub>3</sub> in presence of tartaric acid; precipitation of tungstic acid.

Os. Distillation as OsO<sub>4</sub> from 2 N HNO<sub>3</sub>; precipitation as sulfide.

Ir, Pt. Precipitation of chloroplatinate and chloroiridate by salting out with NH<sub>4</sub>Cl after oxidation with aqua regia; repeated dissolution and salting out in a nonoxidative medium (to avoid precipitation of Pd); boiling with aqua regia to remove Os and Ru completely; separation of Ir by hydrolysis (boiling with BaCO<sub>3</sub>); fractional precipitation of Ir and Pt as metals by means of formic acid.

Au. Extraction from 1.5 N HCl; precipitation with ammonia; precipitation of gold with hydroquinone; reprecipitation with SO<sub>2</sub>.

Hg. Precipitation of HgS, washing with ammonium polysulfide; separation of other Group IV sulfides by dissolution in hot 2 N HNO<sub>3</sub>; distillation of mercury at red heat; precipitation of HgS.

Tl. Extraction of TlCl<sub>3</sub> from 6 N HCl with ether after oxidation of Tl<sup>+</sup> to Tl<sup>3+</sup>; precipitation with excess of ammonia; separation of gold with hydroquinone; precipitation of Tl after reduction with SO<sub>2</sub>.

Pb. Precipitation of PbS; precipitation of PbSO<sub>4</sub>, dissolution in ammonium acetate, and precipitation of PbCrO<sub>4</sub>.

Bi. Precipitation of Bi<sub>2</sub>S<sub>3</sub>, washing with ammonium polysulfide. Separation of AgCl; separation of PbSO<sub>4</sub>, precipitation of BiOCl.

Po. Karraker and Templeton's method of purifying Po [14] was adopted. Experiments showed that in the present case no other comparatively long-lived  $\alpha$ -emitters, apart from Po were formed in appreciable amount. For this reason, Po preparations obtained from the original solution by separation on silver foil or simply by evaporation of a known fraction of the solution showed the same  $\alpha$ -activity as purified preparations.

#### Counting Procedure and Determination of Yields

The preparations prepared for measurement consisted of precipitates, about 10-15 mg in weight, filtered off on flat round filters, 2 cm in diameter, placed on standard aluminum dishes having low sloping sides and perforated bottoms. The dishes were prepared from aluminum foil, 0.5 mm in thickness. The activities of the preparations isolated were measured by suitable counting devices, operated for the necessary periods of time, and yields were calculated from the results obtained.

In order to convert relative yields into the absolute cross section for the formation of the given isotope, monitor aluminum foils were bombarded simultaneously with the target, and in these Na<sup>24</sup> was formed by the reaction Al<sup>27</sup> (p, 3p, n). The cross section for this reaction was taken to be 11 millibarns. The isotope Sr<sup>90</sup> was generally taken as the standard for comparison (it was isolated in every bombardment), and the cross section for its formation was determined from the yield of Na<sup>24</sup> from Al.

Measurements on isotopes that undergo  $\beta$ -decay (mainly fission products — apart from the heaviest fragments, that undergo K-capture and emit positrons) were carried out with a standard end-on counter having a thin mica window.

When necessary, the identification of the isotopes was confirmed by determining the energy of the  $\beta$ -radiation by the absorption method or with a rough  $\beta$ -spectrometer. Measurements of  $\alpha$ -activity were made with the aid of an ionization chamber connected to a linear amplifier.

The most difficult problem was the determination of the yields of isotopes undergoing electron capture with subsequent emission of X-rays and  $\gamma$ -quanta. Such isotopes form most of the spallation products of the reaction studied. In this case, whatever the method of measurement may be, for the exact determination of the yield it is necessary to know the precise way in which the given isotope disintegrates and to have data concerning the energy and number of  $\gamma$ -quanta per act of disintegration and the corresponding conversion coefficients, and also concerning the

ratio of K- to L-capture; it is, moreover, necessary to take account of fluorescence yield and the presence of Auger electrons and of various X-radiation attributable to them. In such a case it is expedient to use various filters in order to isolate the desired form of radiation, for which the intensity (per disintegration event) and counting efficiency in the counting device employed are known. We used two methods of measurement, which could be checked against each other. Counting efficiencies for quanta of electromagnetic radiation varying in hardness have been determined by other authors for the two counting devices that we used [14, 15].

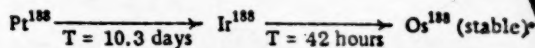
First, we used a standard end-on counter provided with beryllium, aluminum, and lead filters. Second, we used a B-1 cylindrical counter (diameter 10 mm, thickness of aluminum wall 0.1 mm) having an aluminum jacket 3 mm in thickness. Electrons and soft X-rays ( $L_x$ ,  $M_x$ , etc.) were absorbed in this jacket, and only K-rays and  $\gamma$ -quanta were counted in the counter. For this counter we determined the counting efficiency—which included also the geometric factor—for the  $\gamma$ -radiation of a  $\text{Co}^{60}$  preparation (mean energy of  $\gamma$ -quanta 1.25 Mev) having a known number of disintegrations per second. The relative efficiencies of the counter for  $\gamma$ -quanta of other energies were determined from the curve given in the paper [15] for the dependence of efficiency on energy for a counter with an optimum aluminum cathode. All preparations were measured with these two counting devices, and in the majority of cases the results were in satisfactory agreement.

The errors in our calculated values for the production cross sections for the various reaction products are made up of individual errors in the determination of individual factors; some of these are small, but others may be considerable and, moreover, difficult to calculate. However, the agreement found between the values of yields determined by different methods shows that the precautions taken were probably adequate, enabling large errors to be avoided.

## DISCUSSION OF RESULTS

The reaction products isolated and their measured formation cross sections are given in the table and in Fig. 1. With rare exceptions the fission and spallation products formed were found to be radioactive and converted by a definite chain of disintegrations into stable nuclides. It was, therefore, considered to be most expedient to isolate the last members of the active chains, which are generally comparatively long-lived (formed usually from isobars of considerably shorter life) and which pass finally into stable nuclei. The yields of these last members of the chains generally include almost the whole of the yield of all isotopes with the given mass number.

However, we must also take into account the possibility that the last member of the chain may have a comparatively short half-life and may exist at the moment of its isolation as a result of its formation from a predecessor of longer life, e.g.:



In such cases repeated separations of daughter and mother elements were made at different times after the end of bombardment, and this permitted, in particular, the determination of their independent

Fig. 1. Dependence of the yields (in millibarns) of fission and spallation products on the mass numbers of the nuclei formed.

yields. Items in the table that are enclosed in rectangles refer to isotopes whose nuclei are "screened" by stable isobars and are, therefore, obtained in independent yield, so that the yield does not refer to all products of the given mass number. In Fig. 1, points representing these yields are marked by black squares.

The main conclusion that can be derived directly from the experimental results is that the ratio of the cross sections of Bi for fission and spallation reactions is 7% for 660-Mev protons; in accordance with data that we have checked it is 5% for 480-Mev protons.

\* The existence of the isotope  $\text{Pt}^{188}$ , which we discovered in earlier work, has recently been confirmed [17].



TABLE 1

Summary Table of the Measured Cross Sections for the Products

Isotope	$\sigma_{mb}$ 660 Mev		$\sigma$ (660) mean (weighted)	$\sigma$ (480) (cylind- rical counter [10])	$\sigma$ (660)/ $\sigma$ (480) cylindrical counter
	end-on counter	cylindrical counter			
Po 208	—	3.3 ( $\alpha$ )	3.3	3.1	—
Po 206	—	3.0 ( $\alpha$ )	3.0	2.6	—
Bi 206	90	61	75	71	0.85
Bi 205	83	73	78	77	0.9
Pb 203	132	90	110	100	0.9
Tl 202	10	20	15	12.3	1.6
Tl 201	110	140	125	129	1.1
Tl 200	142	140	140	130	1.1
Hg 197	82	86	87	86	1.0
Au 196	2	5	3.5	3.0	1.6
Au 195	22	28	28	26	1.1
Au 194	8	12	10	5.6	2.1
Ir 190	47	—	47	—	—
Ir 188	2.1	—	2.1	—	—
Pt 188	27	—	27	—	—
Os 185	15	14	15	—	—
W 178	2.5	1.8	2.5	0.78	2.3
Ce 134	—	0.42	0.42	0.11	3.8
Ba 128	—	0.3	0.3	0.2	1.5
Ag 111	3.7	—	3.7	3.1	1.2
Mo 99	5.4	—	5.4	4.4	1.23
Sr 89	6.4	6.4	6.4	4.4	1.45
Cu 67	0.86	—	0.86	—	—
Fe 59	—	0.36	0.36	0.15	2.4

Before fission occurs, 15-16 nucleons leave the nucleus. These are mainly neutrons (usually not more than one or two protons, this being confirmed also by experiments on thick-layer plates) [12, 16].

This behavior confirms the emission character of the fission of bismuth by high-speed particles. In our case it appears that Po, Bi, Pb and Tl nuclei, which are highly neutron-deficient, undergo fission preferentially.

The fission fragments are characterized by a neutron-proton ratio of about 1.35, which is in accord with the results of other authors [9]. Fission by rapid particles is, therefore, not accompanied by redistribution of charges in the fragments formed.

It was found that in the spallation of the bismuth nucleus by 660-Mev protons, on the average 2 protons and 8 neutrons are ejected. When the interpolated yields of nonisolated products are taken into account, approximately the same values are obtained. We must point out that this number of protons may be too high, and the number of neutrons correspondingly too low (apparently not more than by unity), owing to the fact that we separated not only the immediate reaction products, but also their daughter products. Unlike the spallation products of light and medium-weight nuclei, those obtained from bismuth were mainly neutron-deficient (compared with stable nuclei).

The formation of stable nuclei is found to be very unlikely (this view is supported also by the low yields of screened isotopes). However, in those cases in which an element has many stable isotopes and the stability region extends to fairly light isotopes of this element (as in the case of Hg and Pt), these light stable isotopes may be obtained directly to an appreciable extent. For certain mass numbers, therefore, it was not possible to determine the yield experimentally, although it could be estimated approximately by interpolation on the curve for the yields.

Fig. 2 shows that the yields of nuclei far-removed from the target nucleus with respect to A and Z increase with increase in the energy of the bombarding particles. At the same time, however, there is also a relative increase in the yields of "screened" nuclei (see table), i.e., nuclei corresponding to enhanced reduction in the charge of the target nucleus (greater  $\Delta Z$ ) for a given fall in the mass number ( $\Delta A$ ).

It must be remembered that the formation of a given nucleus is determined by the total numbers of protons and neutrons knocked out and evaporated in the spallation reaction.\* Thus,

$$\Delta Z = p_k + p_e$$

$$\Delta (A-Z) = n_k + n_e$$

( $p$  is the number of protons,  $n$  the number of neutrons, and  $k$  and  $e$  indicated "knocked out" and "evaporated", respectively). For a given value of  $\Delta A$  the mean value of  $\Delta Z$  will be the greater, the greater the ratio of the number of particles knocked out to the number evaporated, since the ratio  $p_k/n_k$  is, in general, greater than  $p_e/n_e$  (neutrons always predominate greatly in the evaporation component). Hence, as the energy of the particles increases,  $\Delta Z$  (for given  $\Delta A$ ) increases, and the curve for the distribution of the yields of products having given values of  $A$  is displaced in the direction of products less deficient in neutrons.

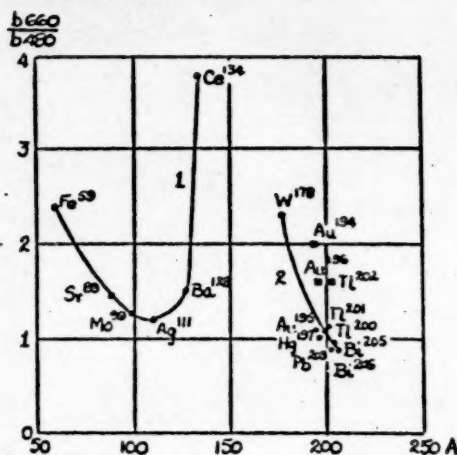


Fig. 2. Ratio of cross sections for 660-Mev and 480-Mev protons in the formation of various products by the bombardment of bismuth nuclei.

evaporation of single protons and neutrons is practically impossible. As can be shown from simple energy considerations, it can occur only as the result of the evaporation of a large number of  $\alpha$ -particles [e.g., a reaction of the form  $\text{Bi}^{209} (p^{130}; 24n) \text{Ce}^{134}$ ], i.e., when there is a very considerable, and therefore very unlikely, departure of the number of  $\alpha$ -particles from the mean. It is possible also that this isotope may be formed as a result of the ejection of larger fragments, which is to a certain extent a variant of the phenomenon of asymmetrical fission. A final solution of the problem must await further experiments.

The spallation products that we observed were formed as the result of a nuclear cascade process which leads to the ejection of several nucleons from the bismuth nucleus (and, if proton capture occurred, from a polonium nucleus) with subsequent emission of further nucleons by evaporation from the excited nucleus. For a given excitation energy  $u$  of the nucleus, the total number of evaporated nucleons can be calculated by an application of the simplest variant of the theory with the aid of the equations:

$$\frac{du}{dA} = \frac{\Gamma_p(\epsilon_p + 2T + V_p) + \Gamma_n(\epsilon_n + 2T) + \Gamma_\alpha(\epsilon_\alpha + 2T + V_\alpha)}{\Gamma_p + \Gamma_n + 4\Gamma_\alpha};$$

$$\frac{\Gamma_p}{\Gamma_n} = \left(1 + \frac{V_p}{T}\right) e^{-\frac{V_p}{T}} \frac{Z}{A-Z};$$

\* The evaporation of  $\alpha$ -particles (which we shall take into account in our further considerations) does not affect the general sense of these discussions.

The fission of nuclei formed from bismuth nuclei as a result of spallation has an emission character [9]; in other words, the neutron breadth  $\Gamma_n$  is greater than the fission breadth  $\Gamma_f$  for nuclei having an excitation energy of  $u \geq 10$  Mev.

Hence, the character of the fission process (and, therefore, also the yield distribution curve for the products) for a nucleus having given values of  $Z$  and  $A-Z$  does not depend on the energy of the bombarding particle (all highly excited states are "removed" by prior evaporation of nucleons). With increase in the energy of the bombarding particle, the relative number of light nuclei undergoing fission increases and the fission yield curve (see Fig. 2) becomes broader and is displaced to lower values of  $A$  and  $Z$ . However, as can be seen from Curve 1 in Fig. 2, with increase in the energy of the bombarding particles there is an increase also in the relative yield of heavy fission products; this can be explained either by the asymmetric character of the fission of neutron-deficient nuclei, or less probably, by a supplementary yield of heavy fragments resulting from the "intrusion" of spallation products into the region of fission products. The formation of these isotopes as a result of the ejection and

$$\frac{\Gamma_{\alpha}}{\Gamma_p} \approx 0.5.$$

( $A$  is the number of nucleons in the nucleus;  $T$  is the temperature of the nucleus ( $u \approx 0.1 AT^2$ );  $\epsilon_x$  is the binding energy of the particles in the nucleus ( $\epsilon_p = \epsilon_n \approx 8$  Mev;  $\epsilon_{\alpha} = -3$  Mev);  $V_{\alpha}$  is the coulomb barrier,  $V_p$  being the barrier for protons;  $\Gamma_p$ ,  $\Gamma_n$ , and  $\Gamma_{\alpha}$  are the respective breadths, proportional to the probabilities for the escape of the particles from the excited nucleus). The ratio  $\Gamma_{\alpha}/\Gamma_p$  was taken as 0.5 (data from the paper [5]).

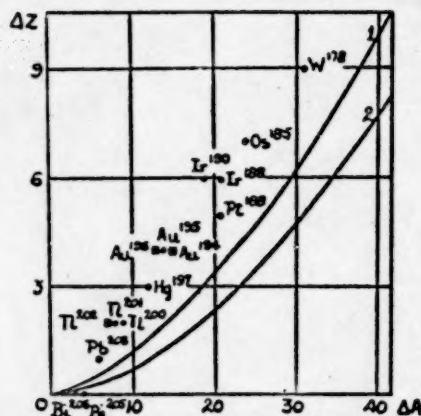


Fig. 3. Dependence of the loss of charge  $\Delta Z$  by the target nucleus  $\text{Bi}_{209}$  on the number ( $\Delta A$ ) of nucleons knocked out and evaporated: 1)  $V_p = 5$  Mev,  $V_{\alpha} = 10$  Mev; 2)  $V_p = 8$  Mev,  $V_{\alpha} = 17.5$  Mev.

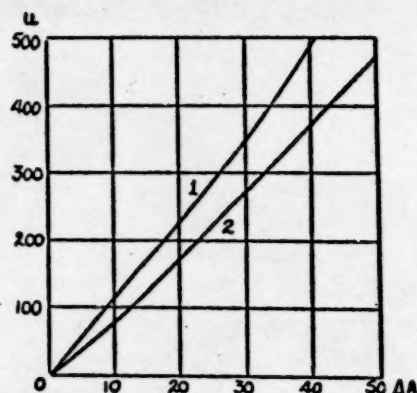


Fig. 4. Dependence of the excitation energy of the nucleus  $u$  on the number of nucleons evaporated ( $\Delta A$ ): 1)  $V_p = 8$  Mev,  $V_{\alpha} = 17.5$  Mev; 2)  $V_p = 5$  Mev,  $V_{\alpha} = 10$  Mev.

It is difficult to estimate the height of the effective barrier ( $V_p$  or  $V_{\alpha}$ ); for strongly excited nuclei it is considerably less than for the nucleus in the ground state [5]. For comparison purposes we made the calculations for two values of each parameter:  $V_p = 8$  Mev,  $V_{\alpha} = 17.5$  Mev and  $V_p = 5$  Mev,  $V_{\alpha} = 10$  Mev (the second case is unlikely to represent actual conditions).

Fig. 3 presents our calculated curves for the dependence of the loss of charge  $\Delta Z$  ( $\Delta Z = 83 - Z$  of the nucleus formed) on the change in mass number ( $\Delta A = 209 - A$  of the nucleus formed). It is clear that  $\Delta A$  is simply the total number of nucleons evaporated. The nuclei that we observed (more accurately, the corresponding experimental points) are represented by circles, against which the symbols of the corresponding isotopes are placed.

An examination of the curves in Fig. 4 shows that the value of  $u$  (and still more  $dA/du$ , see below), expressed as a function of  $\Delta A$ , is not greatly dependent on which variant is chosen for the values of  $V_p$  and  $V_{\alpha}$ .

If we assume that in all cases the Bi nucleus lost five nucleons as a result of the nuclear cascade process before the evaporation process began,\* then it is possible to construct — to a very rough approximation, of course — a curve for the distribution of the probability of excitation of the nucleus to a given energy  $u$  [ $W(u)$  is approximately equal to  $d\sigma_{\text{total}}/du$ , in which  $\sigma_{\text{total}}$  is the total cross section for the nonelastic interaction of a proton with a bismuth nucleus]. It should be noted that

$$W(u) dA = W(u) \frac{dA}{du} du = W'(u) du.$$

\* For 700-Mev protons and a bombarded nucleus having a mass number of about 100, the number of nucleons knocked out (excluding the bombarding proton) is approximately 3 [18]. The number of nucleons knocked out increases comparatively slowly with increase in  $A$ . If we assume that it is proportional to  $A^{2/3}$ , we obtain for a Bi nucleus bombarded with such protons the value of 5-6 ejected nucleons.



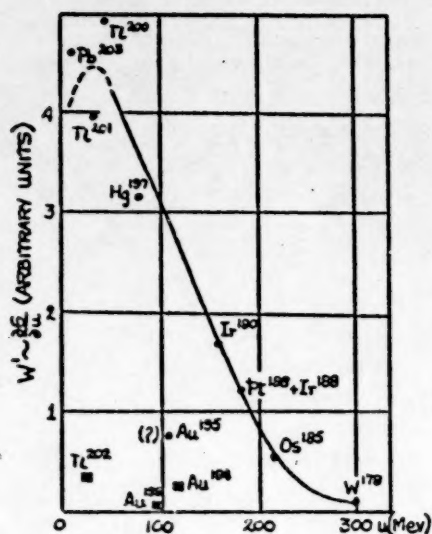


Fig. 5. Density of the probability of the excitation of a nucleus formed from  $\text{Bi}_{83}^{209}$  as a result of a nuclear cascade process ( $E_p = 660$  Mev).

In these equations  $W(u)$  is the density of the probability, calculated per unit interval of mass number;  $W'(u)$  is the probability per unit interval of excitation energy. The values of  $W'(u)$  are found by comparison of the yield curves in Fig. 1 and the lower curve in Fig. 4. The last curve can also yield the corresponding values of the derivative  $dA/du$ .

The results of such transformations are shown in Fig. 5. The mean excitation energy is here found to be about 90 Mev. Choice of the second variant for the values of the parameters  $V_p$  and  $V_\alpha$  leads us to a lower and probably less reliable value of  $u$  (about 70 Mev). The indicated value of  $u$  must be regarded as only a comparatively crude approximation, probably somewhat less than the true value of the mean excitation energy, although it agrees excellently with calculated results [16]. It is probable that in actual fact, the formation of nuclei far-removed in  $Z$  and  $A$  from the target nucleus occurs after the ejection of fewer particles than we have assumed in our calculation (about 5).

In conclusion, it is our pleasant duty to express our deep gratitude to M. G. Meshcheryakov and the operating staff of the synchrocyclotron of the Institute of Nuclear Problems of the USSR Academy of Sciences for help in the performance of the experiments.

## SUMMARY

1. Twenty-four radioactive isotopes of seventeen elements were isolated and identified in the products arising in the bombardment of bismuth with 660-Mev protons.
2. The yields of reaction products were determined. The ratio of cross sections for fission and spallation reactions was found to be about 0.07.
3. The fission reaction is preceded by the ejection, on the average, of 15-16 nucleons. In the spallation reaction 2 protons and 8 neutrons are ejected, on the average.
4. As the energy of the bombarding protons increases there is a displacement of the yields into the stability region and also, probably, an increase in the asymmetry of the fission of strongly excited nuclei. The results permit an estimation of the mean excitation energy of the nuclei formed as a result of the nuclear cascade process, the value found being about 90 Mev.

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## INTERPHASE PARTITION IN SYSTEMS CONTAINING ANOMALOUS MIXED CRYSTALS

### COMMUNICATION 4. THE SYSTEMS $\text{NH}_4\text{Cl}-\text{CuCl}_2-\text{H}_2\text{O}$ AND $\text{NH}_4\text{Cl}-\text{CrCl}_3-\text{H}_2\text{O}$

E. M. Ioffe

We have shown in previous investigations that a good criterion for systems consisting of anomalous mixed crystals and solution is provided by the partition coefficient for the distribution of a microcomponent between the saturated solution and crystals of the second substance. Applying this criterion to systems consisting of ammonium chloride and heavy-metal chlorides, we have shown [1] that in the case of the system  $\text{NH}_4\text{Cl}-\text{FeCl}_3-\text{H}_2\text{O}$  we have a colloidal solid solution, its distinguishing feature being the existence of a lower limit for its formation. The work of Khlopin and Nikitin has established that for the formation of mixed crystals of a new type [2] and of anomalous mixed crystals [3] it is necessary that at the surface of the growing crystal there should be a sufficient number of ions of the second component to form a region of its own crystal lattice. When, however, the concentration of the second component is very low, the probability of a number of simple or complex ions of the second component being found in close array is very slight, and mixed crystals cannot be formed. This implies that in such systems there will be a lower limit for mixed-crystal formation. In the case of true mixed crystals, in which replacement occurs ion for ion or atom for atom, a lower limit for mixed-crystal formation was never observed.

For the system  $\text{NH}_4\text{Cl}-\text{FeCl}_3-\text{H}_2\text{O}$  we showed that when the concentration of iron in the solution falls below a certain value, the partition coefficient for the distribution of iron begins to fall, tending to zero. This proves the existence of a lower limit for mixed-crystal formation in this system containing iron. Before we can claim that the existence of a lower formation limit is a criterion for the differentiation of true from anomalous mixed crystals, it is essential to study a number of typical systems. Study of a system consisting of ammonium chloride and the chloride of a bivalent metal, namely  $\text{NH}_4\text{Cl}-\text{MnCl}_2-\text{H}_2\text{O}$ , showed its great difference from the analogous system containing iron. Whereas in the system  $\text{NH}_4\text{Cl}-\text{FeCl}_3-\text{H}_2\text{O}$  the partition coefficient began to fall at an iron concentration of about  $10^{-2}$  mole/l for the manganese system it remains constant over a wide range of concentrations and down to  $10^{-6}$  mole per liter. Moreover, the actual values of the partition coefficients differ greatly, the value for manganese (0.76) being almost thirty times as great as that for iron (0.026 at its maximum).

The object of the present work was the verification of the conclusions that we had reached from partition studies on the systems  $\text{NH}_4\text{Cl}-\text{FeCl}_3-\text{H}_2\text{O}$  and  $\text{NH}_4\text{Cl}-\text{MnCl}_2-\text{H}_2\text{O}$  through the investigation of analogous systems.

### EXPERIMENTAL

As an analog of the manganese system we selected  $\text{NH}_4\text{Cl}-\text{CuCl}_2-\text{H}_2\text{O}$  because the ionic radius of bivalent copper is very close to that of bivalent manganese and the double salt  $2\text{NH}_4\text{Cl}_2 \cdot \text{MnCl}_2 \cdot 2\text{H}_2\text{O}$  corresponds in composition to the double salt  $2\text{NH}_4\text{Cl} \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .

We made use of the procedure developed by Khlopin [4] and his students for the study of the partition of a microcomponent between solid and liquid phases. There are three ways in which equilibrium may be attained. First, "from below": equilibrium is attained by recrystallization of crystals of the macrocomponent in its saturated solution containing the microcomponent. Second, the mixed crystals may be recrystallized in a saturated solution of the pure macrocomponent. Third, equilibrium may be attained by crystallization from supersaturated solutions with rapid stirring. All that has been written about the methods of attaining equilibrium in the case of true mixed crystals applies also, as our investigations have shown [5], to anomalous mixed crystals. In the present work we used the third method of attaining equilibrium.

One of the objects of the present investigation was, therefore, to determine whether or not a lower limit for mixed-crystal formation exists in the system  $\text{NH}_4\text{Cl}-\text{CuCl}_2-\text{H}_2\text{O}$ . We sought for this limit by determining the partition coefficient for various concentrations of microcomponent in the solution. The partition coefficient  $D$  is most conveniently expressed as follows:

$$\frac{x}{y} = D \frac{100-x}{100-y}$$

( $x$  and  $y$  are the amounts of micro- and macro-components passing into the crystals, expressed as percentages of the total amounts in the system). The system was studied at 0°. Ammonium chloride that had been recrystallized three times was used.

The experiments were generally carried out as follows: the required amount of ammonium chloride crystals was weighed into a glass test tube, about 75 ml in capacity, and to this was added 30 ml of the original solution, which consisted of a solution of ammonium chloride saturated at 0° and containing a definite amount of cupric chloride as microcomponent. The test tube was closed with a ground stopper and heated in hot water until the solid phase had dissolved completely, when it was transferred to a thermostat containing melting ice. The solution was allowed to attain the temperature of the thermostat and was then stirred vigorously with a mechanically driven screw-shaped glass stirrer for four hours. Stirring was then discontinued and the stirrer removed. The crystals were removed from the mother liquor and washed with a solution of ammonium chloride which had been saturated at 0° and which was cooled to 0° before use.

TABLE 1

Amt. of Cu (g) per ml of original solution	Cu concentration (moles per liter)	Amt. of $\text{NH}_4\text{Cl}$ precipitated (%)	Amt. of Cu in crystals (%)	D (according to the crystals)	D (according to the solution)	Method of determining copper
0.00222	$3.5 \cdot 10^{-2}$	30.0	21.2	0.62	—	Colorimetric
0.00222	$3.5 \cdot 10^{-2}$	30.0	20.7	0.61	—	"
0.00044	$7.0 \cdot 10^{-3}$	23.0	13.7	0.53	—	"
0.00044	$7.0 \cdot 10^{-3}$	20.0	12.7	0.56	0.58	"
0.00044	$7.0 \cdot 10^{-3}$	30.0	16.6	0.46	0.43	"
0.00044	$7.0 \cdot 10^{-3}$	30.0	16.2	0.45	—	"
0.00022	$3.5 \cdot 10^{-3}$	30.0	15.1	0.47	0.49	"
0.0000045	$7.0 \cdot 10^{-5}$	30.0	20.4	0.59	—	Colorimetric with preliminary precipitation with hydrogen sulfide
0.0000045	$7.0 \cdot 10^{-5}$	30.0	19.8	0.58	—	
$1.7 \cdot 10^{-5}$	$2.7 \cdot 10^{-4}$	30.0	16.7	—	0.47	
$1.3 \cdot 10^{-5}$	$2.1 \cdot 10^{-4}$	30.0	18.8	0.54	—	Experiments with radioactive copper
				Mean	Mean	
				0.53	0.49	

We followed the partition of the microcomponent between the liquid and solid phases by determining the copper contents of the original solution and the crystals, and sometimes also of the solution after the experiment. For copper concentrations in the range  $3.5 \cdot 10^{-2}$  to  $3.5 \cdot 10^{-3}$  mole per liter we determined copper colorimetrically with the aid of the blue color resulting from the formation of tetrachlorocuprate.

So that we could reduce the concentration of copper in the original solution and still obtain reliable results, we took a liter or more of the solution for each experiment instead of the usual 25-30 ml. In this way we succeeded in determining partition coefficients at a copper concentration of  $7.0 \cdot 10^{-5}$  mole per liter in the original solution. In these experiments we first precipitated the copper with hydrogen sulfide in an acid medium. The calcined precipitate was dissolved in a few drops of hydrochloric acid, the solution was diluted with distilled water and neutralized, and colorimetric analysis was carried out in the usual way. The colorimetric determinations were accurate within 3-4%.

In order that the concentration of copper in the original solution might be reduced still further we went over to radiometric methods of analysis. For this purpose we used one of the radioactive isotopes of copper, namely  $\text{Cu}^{64}$ , which has a half-life of 12.8 hours. Measurements were carried out on the  $\beta$ -emission with a Type B apparatus fitted with a  $\text{B}_1$  tube. The results obtained are shown in Table 1, in which  $D$  is the partition coefficient

The results show that for copper concentrations in the original solution ranging from  $10^{-2}$  to  $10^{-7}$  mole per liter the numerical value of the partition coefficient remains constant, being on the average 0.53 according to the crystals and 0.49 according to the solution.



$A_5$  an analog of the system  $NH_4Cl-FeCl_3-H_2O$  we selected the system  $NH_4Cl-CrCl_3-H_2O$ . Partition in this system was studied by the same methods as those used for the copper system, i.e., equilibrium was attained by crystallization from supersaturated solutions with rapid stirring. The system was studied at  $0^\circ$ .

The very first experiments showed that the coefficient for the partition of chromium between solid and liquid phases is extremely small in this system and it is necessary to use a radioactive indicator even with fairly high concentrations of chromium in the original solution. For this purpose we used one of the radioactive isotopes of chromium, namely  $Cr^{51}$ , which has a half-life of 26.5 days. Measurements were carried out on the  $\beta$ -emission with a Type B apparatus fitted with a  $B_1$  tube. The original solutions were saturated with ammonium chloride at  $0^\circ$  and contained various amounts of chromic chloride as microcomponent.

The partition of chromium between liquid and solid phases was followed by analysis of the crystals only, and this was carried out as follows: the crystals were carefully dried in a silica beaker on a sand bath, treated with strong nitric acid, and left on the bath until removal of ammonium chloride was complete. The residue in the beaker was carefully dissolved in water, and the solution, which contained chromic chloride, was transferred a drop at a time to an aluminum dish, where it was evaporated with the aid of an infrared lamp. The activity of the crystals was measured with a  $\beta$ -ray counter. The activity of the original solution was determined in the same way.

The concentration of chromium in the original solution was determined gravimetrically by precipitation as hydroxide, calcination, and weighing as  $Cr_2O_3$ . The results are given in Table 2.

TABLE 2

Amt. of Cr (g) per ml of orig- inal solution	Cr concentration (moles per liter)	Amount of		D	Activity taken for experiment ( $\mu$ - pulses)	Activity in the crystals (impulses)
		$NH_4Cl$ in crystals (%)	Cr in cry- stals (%)			
0.0291	$5.6 \cdot 10^{-1}$	30	0.11	0.0026	473,500	537
0.0291	$5.6 \cdot 10^{-1}$	30	0.08	0.0020	470,000	360
0.0204	$4.0 \cdot 10^{-1}$	30	0.10	0.0023	159,600	160
0.0151	$2.9 \cdot 10^{-1}$	30	0.12	0.0028	77,500	96
0.0151	$2.9 \cdot 10^{-1}$	30	0.09	0.0021	75,000	66
0.0135	$2.6 \cdot 10^{-1}$	30	0.08	0.0020	168,850	128
0.0135	$2.6 \cdot 10^{-1}$	30	0.09	0.0021	177,100	162
0.0115	$2.2 \cdot 10^{-1}$	30	0.11	0.0026	601,250	630
0.0115	$2.2 \cdot 10^{-1}$	30	0.10	0.0023	300,625	296
			Mean	0.0023		
0.0025	$4.8 \cdot 10^{-2}$	30	0.04	0.0010	73,650	27
0.0025	$4.8 \cdot 10^{-2}$	30	0.05	0.0012	73,620	38
0.0025	$4.8 \cdot 10^{-2}$	30	0.06	0.0014	69,225	40
0.0024	$4.6 \cdot 10^{-2}$	30	0.04	0.0010	51,450	23
0.0024	$4.6 \cdot 10^{-2}$	30	0.05	0.0011	51,450	29
			Mean	0.0011		
0.00044	$8.4 \cdot 10^{-3}$	30	Mixed crystals are not formed		26,875	2
					26,875	3

The first series of experiments was carried out on solutions containing from 0.0291 to 0.0115 g of chromium per ml of solution. Over this range of concentrations the partition coefficient  $D$  remains constant in spite of a 2.5-fold reduction in the chromium content of the solution; its average value is 0.0023. In the second series of experiments the chromium content of the original solutions was 0.0025 g/ml, i.e., was further reduced in the ratio 1.4.6. Table 2 shows that the partition coefficient is reduced to about one-half of its value in the previous series of experiments, i.e., to 0.0011, on the average. The last series of experiments was carried out on an original solution containing 0.0044 g of chromium per ml of solution. In these experiments all of the chromium remained in the solution, whereas 30% of the ammonium chloride taken passed into the precipitate. Hence, when the chromium concentration is reduced from 0.0291 to 0.00044 g/ml, the partition coefficient falls from its maximum value to zero, so that in this system there is a lower limit for the formation of mixed crystals.

Work with this system is greatly complicated as a result of the very low value of the partition coefficient, and reliable results can be obtained only by using preparations of very high specific activity. In order to compare the behaviors of all four systems, consisting of ammonium chloride with the chlorides of trivalent iron and chromium

TABLE 3

Concentration of Fe, etc. (moles per liter)	C <sub>M</sub>	D (mean)	D (% of maximum)	D maximum (mean)
The System NH <sub>4</sub> Cl-FeCl <sub>3</sub> -H <sub>2</sub> O				
0.27	0.57	0.026	94.6	0.0275
0.055	1.26	0.029	105.5	
0.017	1.77	0.015	54.6	
0.0059	2.23	0.005	18.2	
The System NH <sub>4</sub> Cl-CrCl <sub>3</sub> -H <sub>2</sub> O				
5.6 · 10 <sup>-1</sup>	0.25	0.0023	100.0	0.0023
2.7 · 10 <sup>-1</sup>	0.57	0.0023	100.0	
2.2 · 10 <sup>-1</sup>	0.66	0.0024	100.5	
4.8 · 10 <sup>-2</sup>	1.32	0.0011	48.0	
The System NH <sub>4</sub> Cl-MnCl <sub>2</sub> -H <sub>2</sub> O				
4.0 · 10 <sup>-3</sup>	2.40	0.73	92.3	0.80
8.0 · 10 <sup>-4</sup>	3.10	0.76	95.0	
3.4 · 10 <sup>-4</sup>	3.47	0.78	97.5	
6.6 · 10 <sup>-5</sup>	4.18	0.87	108.7	
4 · 10 <sup>-5</sup>	4.40	0.75	93.8	
4 · 10 <sup>-6</sup>	5.40	0.89	111.3	
The System NH <sub>4</sub> Cl-CuCl <sub>2</sub> -H <sub>2</sub> O				
3.5 · 10 <sup>-2</sup>	1.45	0.61	115.0	0.53
7 · 10 <sup>-3</sup>	2.46	0.50	94.3	
2.7 · 10 <sup>-4</sup>	3.6	0.47	97.9	
7.0 · 10 <sup>-5</sup>	4.15	0.58	109.4	
2.3 · 10 <sup>-7</sup>	6.7	0.54	101.9	

and bivalent manganese and copper, we shall represent the results graphically, taking as abscissas the negative logarithms of the molar concentrations of the microcomponent in the solution ( $C_M$ ), and as ordinates - partition coefficients  $D$  expressed as percentages of their maximum values in the various systems. When the results are represented in this way, a clear indication is given of the dependence of the partition coefficient of the microcomponent on its concentration in the solution, and curves that are fully comparable with one another are obtained in spite of the fact that the values of the partition coefficients differ very greatly among themselves.

Curves representing the dependence of the partition coefficient of the microcomponent on its concentration in the solution are shown in Fig. 1.

Curve 1, which is for the iron system, is at first parallel to the axis of abscissas, which indicates that in spite of a reduction in the iron content of the solution the partition coefficient

remains constant. However, at a certain concentration the partition coefficient begins to fall, so that the curve proceeds at an angle to the axis of abscissas. Curve 2, which shows the dependence of the partition coefficient of chromium on its concentration in the solution, proceeds like the iron curve, remaining in the first place parallel to the axis of abscissas; in spite of a reduction in concentration to less than one-half of the original value. With further reduction of the chromium content of the original solution, the partition coefficient begins to fall sharply, so that the curve proceeds at an angle to the axis of abscissas. The curve showing the dependence of the partition coefficients of bivalent manganese and copper on concentration is quite different in character from the curves for trivalent-metal chlorides which we have just considered: whereas in the iron and chromium systems the partition coefficients begin to fall when the concentration of the microcomponent in the solution is of the order of  $10^{-2}$  mole per liter, in the manganese system over a concentration range of approximately  $10^{-3}$  to  $10^{-6}$  and in the copper system from  $10^{-2}$  to  $10^{-7}$  mole per liter, the partition coefficient remains constant. Fig. 1 shows that the curve for the manganese and copper systems is a straight line parallel to the axis of abscissas.

Comparing the partition behavior in the systems  $NH_4Cl-MnCl_2-H_2O$  and  $NH_4Cl-CuCl_2-H_2O$ , we see that they behave in completely analogous ways. If in these systems there is a lower limit for the formation of mixed crystals, then it lies below the range that we have studied.

Most authors consider that the guest component in the manganese system is the complex anion  $(MnCl_4 \cdot 2H_2O)^{-}$  [6]. It is probable that in the copper system the guest component is the complex anion  $(CuCl_4 \cdot 2H_2O)^{-}$ . We consider that the views of Greenberg and Walden [7] are sound and are supported by reliable experimental data. These authors studied the structure of the double salt  $2NH_4Cl \cdot MnCl_2 \cdot 2H_2O$  by means of X-ray analysis and showed that it greatly resembled the structure of  $NH_4Cl$  and could be derived from the latter as follows. We take



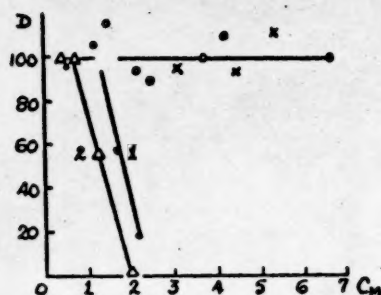


Fig. 1. ● = Fe; Δ = Cr; X = Mn; ○ = Cu.

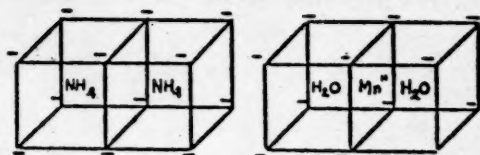


Fig. 2.

two elementary cells of  $\text{NH}_4\text{Cl}$  having a common plane and consisting of 12 chloride ions and 2 ammonium ions disposed at the centers of the two elementary cubes taken (Fig. 2). Two elementary cells of  $\text{NH}_4\text{Cl}$  having a common plane and having 12 chloride ions at the corners and 2 ammonium ions at the centers of the cubes are changed little in dimensions and electrical field when the two ammonium ions are replaced by water molecules and a manganese ion is placed in the center of the square of four chloride ions in the plane that is common to the two cells. Greenberg and Walden explain the formation of mixed crystals by the possibility of the replacement of the group  $2\text{NH}_4^+ \cdot 4\text{Cl}^-$  in the  $\text{NH}_4\text{Cl}$  lattice by the complex anion  $(\text{MnCl}_4 \cdot 2\text{H}_2\text{O})^-$ . If, in fact, such a replacement occurs, then in this case there should not be a lower limit for mixed-crystal formation.

We consider that, if all these considerations are valid for the manganese system, then they should apply also to the copper system, since the radius of a copper ion is such that it may be placed within the ammonium chloride lattice in the same way as the manganese ion. By analogy with manganese, we consider that in the copper system the guest component is the complex anion  $(\text{CuCl}_4 \cdot 2\text{H}_2\text{O})^-$ . Similar replacements cannot, however, occur in the systems  $\text{NH}_4\text{Cl}-\text{FeCl}_3-\text{H}_2\text{O}$  and  $\text{NH}_4\text{Cl}-\text{CrCl}_3-\text{H}_2\text{O}$ , since the complex anions  $(\text{FeCl}_5 \cdot \text{H}_2\text{O})^-$  and  $(\text{CrCl}_5 \cdot \text{H}_2\text{O})^-$  contain five chlorine atoms, which is one too many. This fact is bound to be reflected in the structure of the mixed crystals.

Although mixed crystals formed by ammonium and ferric chlorides have been studied in various aspects by many workers [6], there are only a few references in the literature to the chromium system. Retgers [8] obtained mixed crystals by crystallizing ammonium chloride from an aqueous solution containing chromic chloride, the latter being trapped by the solid phase in very small amount. Moreover, Johnsen [9] states that ammonium chloride crystallized from a solution containing chromic chloride is green in color. With regard to the double salts formed between ammonium chloride and chromic chloride, Larsson [10] has obtained a salt of composition  $\text{NH}_4\text{Cl} \cdot \text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , and Neumann [11] has prepared the double salt  $2\text{NH}_4\text{Cl} \cdot \text{CrCl}_3 \cdot \text{H}_2\text{O}$  or  $(\text{NH}_4)_2[\text{CrCl}_5 \cdot \text{H}_2\text{O}]$ , which Werner [12] and others represent as  $[\text{Cr}(\text{H}_2\text{O})\text{Cl}_5(\text{NH}_4)_2]$ .

Whereas for the system  $\text{NH}_4\text{Cl}-\text{FeCl}_3-\text{H}_2\text{O}$  many authors have shown convincingly that the guest component is the complex anion  $(\text{FeCl}_5 \cdot \text{H}_2\text{O})^-$ , this question has not been finally settled for the chromium system. By analogy with iron, however, it may be supposed that the guest component in the chromium system is the complex anion  $(\text{CrCl}_5 \cdot \text{H}_2\text{O})^-$ , and this view is supported by the similarity in the curves for the dependence of partition coefficient on concentration of microcomponent (iron or chromium) in the solution. Further support is afforded by the results of experiments devised to determine the behavior of two or more microcomponents when simultaneously present in a solution from which anomalous mixed crystals are formed. The experiments showed that the presence of cupric chloride in the solution had no effect on the partition of chromium between liquid and solid phases, whereas the presence of  $\text{FeCl}_3$  had a substantial effect on the value of the partition coefficient: its mean value was increased by a factor of 2.5. In this connection it should be noted that the form of the curve for the dependence of the partition coefficient on the concentration of microcomponent in the solution remained unchanged. From these considerations it may be concluded that the guest component in the chromium system is the complex anion  $(\text{CrCl}_5 \cdot \text{H}_2\text{O})^-$ , which is deposited during crystallization on prepared regions of the lattice formed by the isomorphous complex anion  $(\text{FeCl}_5 \cdot \text{H}_2\text{O})^-$ , this being the reason for the increase in the partition coefficient of chromium.

## SUMMARY

1. Data relating to the partition of small amounts of a substance between the liquid and solid phases in systems consisting of ammonium chloride and the chlorides of the trivalent metals chromium and iron indicate that there is a lower limit for the formation of the mixed crystals  $\text{NH}_4\text{Cl}-\text{FeCl}_3$  and  $\text{NH}_4\text{Cl}-\text{CrCl}_3$ , and that these mixed crystals are colloidal in nature.

2. Partition in systems consisting of ammonium chloride and the chlorides of the bivalent metals manganese and copper is characterized by a partition coefficient that has a constant value over a wide range of concentrations.

3. Greenberg and Walden's scheme provides a satisfactory explanation of the difference in behavior between the chlorides of bivalent Mn and Cu and those of trivalent Fe and Cr when undergoing partition between the saturated solution and crystals of ammonium chloride.

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## SURFACE AND SORPTION PROPERTIES OF ACTIVE CARBONS

### COMMUNICATION 1. SORPTION ISOTHERMS FOR BENZENE AND WATER VAPOR

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The results of chemical analysis show that the organic matter present in active carbons consists essentially of carbon. When carbons are subjected to activation or thermal treatment at sufficiently high temperatures, the carbon content may attain 98-99%.

When kept and applied under the usual conditions, active carbons are in contact with air and are to some extent moist. As a result of activated adsorption and chemisorption of oxygen, at the surface of the carbon there are chemically bound oxygen atoms, which form surface oxides, the composition and properties of which depend on the temperature conditions of the interaction of oxygen with the carbon [1-3]. With prolonged keeping slow oxidation of the surface continues with formation of acidic surface oxides [4]. According to the experiments of Pierce and coworkers, active carbons slowly react with sorbed water with formation of surface oxygen complexes [5].

From these observations we may conclude that under normal conditions the surface of active carbons does not consist only of carbon atoms, but is oxidized to some extent. In the oxidation a condition of equilibrium is probably not attained, and slow further oxidation of the active-carbon surface will occur. The final oxidation product, carbon dioxide, is gradually desorbed from the carbon.

In the general case, the sorption of vapors by active carbons depends on the chemical nature and porous structure of the adsorbent. The effect of surface oxides on the sorption of vapors by active carbons has been studied by Bruns [6] and by us [7, 8]. The polar properties of the surface oxides, which behave like unimolecular layers, affect the components of the adsorption forces in different ways. As our experiments [7] show, the surface oxides have an insignificant effect on the dispersive interaction of the molecules of nonpolar substances such as benzene with the carbon surface. In the adsorption of polar molecules such as methanol and water, however, the surface oxides modify the character of the adsorption considerably in the initial sections of the isotherm, particularly when dispersion forces play a relatively small part in adsorptive interaction. The most notable example is provided by the adsorption of water vapor on active carbons [9].

One of the methods of studying the effect of the nature of the surface of the adsorbent on adsorption is based on varying the chemical nature of the surface of the active carbon while maintaining its porous structure practically unchanged. A study of sorption over a wide range of equilibrium pressures, right up to saturation, makes it possible, in principle, to evaluate the relative values of the surface coverage and pore volume in the sorption of water vapor. The slow change in the chemical nature of the surface of the carbon resulting from its oxidation also has a certain practical interest, since it may be associated with the changes occurring in the sorption properties of active carbons during keeping.

These considerations make it necessary to carry out further, more systematic investigations in this field. In the present investigation we have attempted to determine in greater detail the dependence of the sorptive properties of active carbon on the extent of the oxidation of its surface, the structure of the carbon being maintained practically constant.

### EXPERIMENTAL

1. The active carbon taken for investigation was granulated material obtained under laboratory conditions from coal; it had a bulk density of  $\Delta = 0.640$  g/cc and an ash content of 15.98%. The carbon was ground, and the fraction of grains retained during sieving between sieves having circular openings 1.25 and 1.50 mm in diameter, respectively, was used for the preparation of oxidized carbons (Carbon A).

The main object of the investigation was a study of the sorptive properties of carbons having different amounts of acidic surface oxides, but practically constant in porous structure. As the oxidation of a carbon with atmospheric oxygen is accompanied by a substantial combustion loss, which results in changes in structure, there was no point in



comparing the properties of the original active carbon A and its oxidation products. A carbon having no acidic surface oxides and close in structure to the oxidized carbon may be prepared by thermal treatment of the latter in a vacuum at about 1000° [7].

Samples of oxidized carbons were prepared both from the original ash-containing carbon A and also from carbon freed from ash by double treatments with hydrochloric and hydrofluoric acids followed by careful washing with distilled water until the reaction for chloride was negative. The carbon, after drying, had an ash content of 0.61%. After a repeat of this cycle of treatments with hydrochloric and hydrofluoric acids and careful washing, the dried carbon had an ash content of 0.16% (Carbon B).

The carbons A and B were oxidized at 450° with moist air (humidified by passage through a Drechsel bottle containing water) in the rotating retort already described [10]. A 2 g sample of carbon was taken, and the rate of passage of air was 6 cc per minute per gram of carbon. By variation of the length of treatment it was possible to obtain samples of carbon having different contents of acidic surface oxides (Shilov carbon oxides).

An index of the amount of acidic surface oxides formed was provided by the extent to which caustic soda was adsorbed from aqueous solution. To measure this adsorption 10 ml of 0.023 N NaOH was added to a 0.4 g sample of the carbon contained in a test tube fitted with a ground stopper. The mixture was agitated for one hour and then centrifuged, and the equilibrium concentration of the solution  $c$  was determined by titration to phenolphthalein. The extent of adsorption was expressed in relative units, namely, as the percentage change in the concentration:

$$a = \frac{(c_0 - c)}{c_0} \cdot 100\% \quad (1)$$

( $c_0$  is the initial concentration of the solution).

In order to decompose the acidic surface oxides, a sample of oxidized carbon was heated at 950° in a silica tube closed at one end and evacuated down to a few microns of mercury by means of an oil pump. Air was admitted to the tube only after the carbon had cooled. The duration of the thermal treatment of the carbon was established experimentally with the aid of the following experiments. For the oxidized carbon A1 the alkali adsorption was 33.3%. Heating of the carbon for one hour lowered the alkali adsorption to 1.33%, and heating for two hours lowered it to less than 0.01%. On the basis of these preliminary experiments, all samples of oxidized carbon were heated for two hours. The carbons obtained were preserved in sealed glass test tubes.

The principal data relating to the carbons investigated are presented in Table 1.

TABLE 1

Conditions of Preparation and Designation of the Carbon Samples

Original carbon	Air oxidation of carbon at 450°				Thermal treatment of carbon at 950°		Designation of carbon obtained
	time $t$ (hours)	combustion loss $\omega$ (%)	relative reactivity $\beta$ (hour <sup>-1</sup> )	adsorption of NaOH (%)	yield of carbon (%)	adsorption of NaOH (%)	
A	2.0	10.3	0.052	33.3	—	—	A1
A	3.5	18.7	0.053	45.7	—	—	A2
A1	—	—	—	—	90	0.00	A3
A2	—	—	—	—	90	0.00	A4
B	1.5	9.3	0.062	46.8	—	—	B1
B	2.7	22.3	0.082	56.7	—	—	B2
B1	—	—	—	—	85	0.00	B3
B2	—	—	—	—	85	0.00	B4

The rate of combustion of the carbon in the oxidation process is characterized by the relative reactivity  $\beta$ :

$$\beta = \frac{\omega}{t} \text{ hour}^{-1} \quad (2)$$

( $\omega$  is the combustion loss of the carbon as a fraction, and  $t$  is the duration of oxidation in hours).

The experimental results show that carbon B, which had been freed from ash, was appreciably more reactive to oxygen at 450° than the original carbon A. It is probable that in this case the removal of ash results in some increase in porosity, leading to enhanced reactivity; the ash components themselves are without appreciable catalytic action in the oxidation process.

The oxidation of carbon with atmospheric oxygen at 450°, which is associated with a substantial combustion loss (up to 20% in our experiments), results in the formation of acidic surface oxides, which, as a result of hydration, form surface carboxyl groups. The presence of these groups is the cause of the adsorption of alkali by ion exchange ( $H^+$  exchanged for  $Na^+$ ). The adsorptive power of oxidized carbons with respect to caustic soda increases with increase in the combustion loss of the carbon and is appreciably higher for oxidized carbons obtained from de-ashed carbon.

According to the data in Table 1, when oxidized carbons are treated in a vacuum at 950° with the object of breaking down the acidic surface oxides, the carbons lose 10 to 15% in weight, i.e., there is a peculiar sort of combustion loss. At first sight such combustion losses appear excessively high, but they are in accord with the results of one of our earlier investigations [3].

According to elementary analysis, 2.8% of oxygen was present in an active carbon obtained from sugar (sample No. 23 in the paper cited), which was prepared at a fairly high temperature (1000°) by activation with carbon dioxide until the combustion loss was 48%. When this carbon was oxidized with atmospheric oxygen at 500° until the combustion loss was about 15% (sample No. 26), the oxygen content was raised to 11.7%. Acidic surface oxides were formed on the carbon, and these caused a considerable adsorption of caustic soda from aqueous solution (1.61 millimoles per gram at an equilibrium concentration of 100 millimoles per liter).

When the carbon was treated at 950° in a vacuum, much of the oxygen chemically bound in the form of surface oxides was removed as carbon dioxide. If it is assumed that the product of the thermal treatment contained its original amount of oxygen (2.8%), then it is easy to calculate the algebraic loss in weight of the carbon in the thermal treatment (12.7%). This estimated value is within the limits of the range of "combustion losses" of the carbon samples studied.

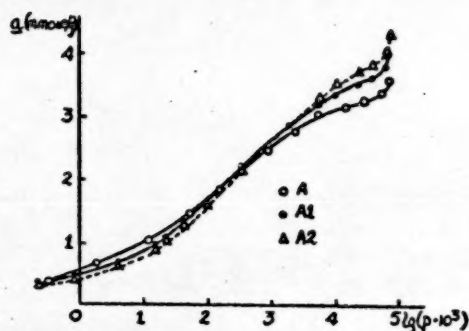


Fig. 1. Isotherms for the sorption of benzene vapor at 20° (semilogarithmic plot) for the carbons: O = A; O = A1; Δ = A2.

B differed little from the isotherm for the original carbon A, particularly in the region of low and medium equilibrium pressures. At higher equilibrium pressures, however, the further activation of the carbons by atmospheric oxygen in the oxidation process causes a substantial increase in the sorption.

By way of example, adsorption isotherms are shown in Fig. 1 as semilogarithmic plots for the original active carbon A (and products A1 and A2), of its activation to different combustion losses. As a result of oxidation there is an appreciable change in the sorptive properties of the carbon, which is associated with change in porous structure. On the other hand, the thermal breakdown of the acidic surface oxides at 950° permits us to convert carbons A1, A2, B1, and B2 into A3, A4, B3, and B4, which have a normal condition of surface, do not contain acidic surface oxides, and have practically identical sorptive properties with respect to benzene vapor. As a typical example

The thermal treatment of oxidized carbons in a vacuum at 950° for two hours results in almost complete breakdown of the acidic surface oxides. The amount of alkali adsorbed becomes immeasurably small (less than 0.01%). As later experiments show, the porous structures of the oxidized carbon and the product of its thermal treatment do not differ to an appreciable extent.

2. As an example of a nonpolar vapor we chose the vapor of benzene. We measured the sorption isotherms for benzene vapor at 20° by the sorption-balance vacuum method over a wide range of equilibrium pressures [11]. The preliminary degassing of the carbons was carried out at 450° with evacuation by a three-stage mercury pump over a period of seven hours. At the end of this period the mercury "stuck" in the capillary of the McLeod gage.

In their general character, the sorption isotherms for benzene vapor adsorbed on carbons of series A and

we compare the sorption isotherms for carbons B1 and B3 (Fig. 2). We may conclude that the isotherms for the de-ashed carbons of series B coincide completely. In the case of the ash-containing carbons of Series A there is a slight but measurable difference between samples having acidic surface oxides and the corresponding samples having a normal condition of surface.

The active carbons of series A and B are adsorbents of the first structural type, containing relatively fine micropores having fairly high adsorption potentials [12]. For such carbons the following adsorption isotherm is applicable:

$$a = \frac{W_0}{v} e^{-B \frac{T^2}{\beta^2} (\log p_s/p)^2} \quad (3)$$

( $W_0$  and  $B$  are constants of the equation,  $v$  is the volume of a millimole of the substance being adsorbed in the liquid state, and  $\beta$  is the affinity coefficient). For benzene, which is taken as the standard vapor,  $\beta = 1$ . Table 2 gives the constants of Equation 3 for the original carbon A and the samples of active carbon of series B.

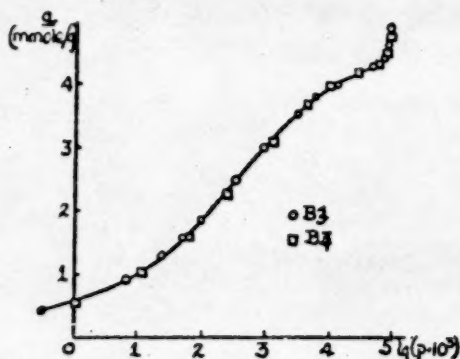


Fig. 2. Isotherms for the sorption of benzene vapor at 20° (semilogarithmic plot) for the carbons: O = B3; □ = B4.

TABLE 2

Constants of the Adsorption Isotherm Equation

Carbon	$W_0$ (cc/g)	$B \cdot 10^5$	Range of applicability ( $p/p_s$ )
A	0.281	0.961	$5 \cdot 10^{-5} - 0.2$
B1	0.370	1.10	$3 \cdot 10^{-5} - 2 \cdot 10^{-2}$
B3	0.350	1.09	$3 \cdot 10^{-5} - 4 \cdot 10^{-2}$
B2	0.345	1.10	$3 \cdot 10^{-5} - 6 \cdot 10^{-3}$
B4	0.350	1.09	$3 \cdot 10^{-5} - 4 \cdot 10^{-2}$

As compared with the original carbon A, all of the de-ashed carbons of series B have an appreciably higher limiting adsorption space  $W_0$ , an effect that is to be attributed mainly to the removal of ash from the carbon and to a supplementary activation effect. For each pair of carbon samples — B1 and B3, and B2 and B4 — which differ in the chemical nature of the surface, the constants  $W_0$  and  $B$  are very close in value. This confirms that the adsorptive power of a carbon for the vapor of a nonpolar substance is almost independent of the degree of oxidation of its surface.

The almost exact coincidence of the benzene-vapor sorption isotherms for each pair of comparable carbon samples, i.e., A1 and A3, A2 and A4, B1 and B3, and B2 and B4, indicates that their porous structures are identical to a sufficiently close approximation. It follows that, to the same degree of approximation, the volumes of the micropores and transitional pores are the same for the two members of each pair.

3. As an example of a polar vapor we chose water. In the gas state water molecules are not associated; in the liquid state association occurs mainly as a result of the formation of hydrogen bonds between the molecules.

The sorption and desorption isotherms were measured for water vapor at 20° by the sorption-balance vacuum method. The conditions used in the preliminary degassing of the active carbons did not differ from those used in the experiments with benzene vapor. In Figs. 3 and 4 we give, by way of example, the sorption and desorption isotherms for water vapor on the oxidized carbons A2 and B2 and on the corresponding thermally treated samples, the acidic surface oxides of which have been broken down (A4 and B4, respectively). The isotherms for the carbons A1, A3 and B1, B3 are similar in character.

For all of the carbons studied the sorption and desorption isotherms are S-shaped. The first part of the sorption branch of the sorption isotherm for the oxidized carbons A2 and B2, which is concave and extends to  $p/p_s = 0.4$ , rises fairly steeply, indicating relatively high adsorption, even in the region of low equilibrium pressures. In the region of medium relative pressures (0.4-0.6), there is a steeper, almost linear rise of adsorption with pressure.



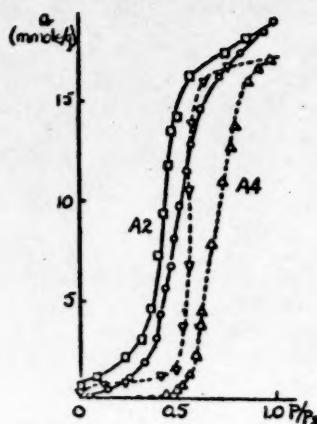


Fig. 3. Sorption and desorption isotherms for water vapor at 20° on carbons A2 and A4.

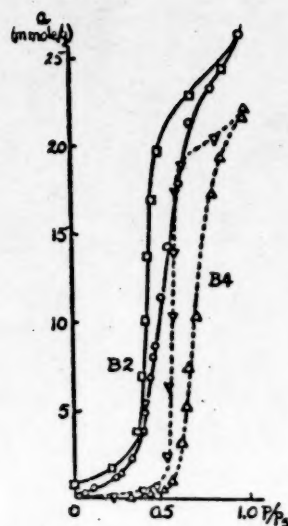


Fig. 4. Sorption and desorption isotherms for water vapor at 20° on carbons B2 and B4.

In the region of high relative pressures (0.6-1.0) the isotherm becomes somewhat less steep, although the extent of adsorption still increases fairly rapidly with rise in pressure.

For the carbon samples A4 and B4, which are analogous in porous structure but do not contain acidic surface oxides, the extent of adsorption in the initial region (relative pressures up to 0.4) is small, being at the limit of measurement. As the pressure rises above  $p/p_s = 0.45$ , there is a sharp rise in the sorption branch, which then has a long linear portion. As the carbon approaches a state of saturation, the curve becomes somewhat less steep. The limiting sorption at a relative pressure of unity is substantially lower for carbons freed from acidic surface oxides.

For all of the carbons studied the desorption branches of the isotherms are, in general, analogous in form to the sorption branches in the regions of medium and high relative pressures. However, the almost linear portions of the desorption branches rise more steeply, and in the range of relative pressures from 0.7 to 1.0 the curves are less steep, particularly for the carbon A4.

For the ash-containing carbons A1, A3 and A2, A4 there is marked irreversibility in the initial region of the isotherm. When the carbon samples are subjected to a vacuum at 20°, they retain an appreciable amount of the more firmly bound water. Removal of ash does not greatly reduce the irreversibility of the sorption, particularly for the samples B3 and B4. Unlike the adsorption isotherms for active carbons derived from sugar, those for the carbons of series A and B have no initial reversible section. The residual ash content of about 0.2% is probably the source of the irreversibility of the initial parts of the isotherms for carbons of series B.

From the isotherms shown in Figs. 3 and 4 it may be concluded that oxidation of the surface of the carbon with formation of acidic surface oxides results in a displacement of the almost linear sections of the main rise in the sorption and desorption branches of the isotherms into the region of lower relative pressures. Breakdown of the acidic surface oxides without substantial change in the porous structure of the carbon results in considerably lower limiting sorption values.

In conclusion, it is of interest to compare the limiting sorption volumes for water vapor  $V_{H_2O}$  with the volumes of the micropores of the carbons and with the sums of the volumes of the micropores and transitional pores, which, by definition, are the limiting sorption volumes for benzene vapor  $V_{C_6H_6}$  [13]. The limiting sorption volumes were calculated from the formula:

$$V_s = a_s \cdot V. \quad (4)$$

( $a_s$  mmoles/g is the limiting sorption at  $p/p_s = 1$  and  $V$  is the volume of 1 mmole of the substance being adsorbed, in the liquid state). The comparison of these quantities is made in Table 3.

The data in Table 3 show that, for the carbon samples A3, A4, B3, and B4, which do not contain acidic surface oxides, the limiting sorption volumes for water vapor coincide with the volumes of the micropores of the active carbons within the limits of experimental error. We have stressed this conclusion in several of our papers [8]. For the oxidized carbons A1, A2, B1 and B2, the limiting sorption volumes for water vapor exceed the volumes of

TABLE 3

Comparison of the Limiting Sorption Volumes of Water Vapor with the Volumes of the Pores of the Active Carbons

Carbon	$\alpha_{\text{H}_2\text{O}}$ (mmole/g)	$V_{\text{H}_2\text{O}}$ (cc/g)	$V_{\text{mi}}$ (cc/g)	$V_{\text{C}_6\text{H}_6} = V_{\text{mi}} + V_{\text{n}}$ (cc/g)	$V_{\text{H}_2\text{O}}/V_{\text{C}_6\text{H}_6}$
A1	17.59	0.318	0.305	0.356	0.895
A3	17.05	0.308	0.304	0.351	0.878
A2	18.90	0.342	0.317	0.382	0.896
A4	17.15	0.310	0.314	0.368	0.843
B1	22.31	0.403	0.361	0.446	0.903
B3	19.78	0.357	0.368	0.438	0.817
B2	26.38	0.476	0.415	0.526	0.897
B4	21.90	0.396	0.396	0.503	0.788

the micropores of the active carbons, but the limiting sorption volumes for benzene vapor are considerably less. These results are of significance in relation to peculiarities in the sorption of water vapor on active carbons differing in the nature of their surfaces.

#### DISCUSSION OF THE EXPERIMENTAL RESULTS

The main object of the present investigation was the determination of the effect of the chemical nature of the surface of active carbons on their sorption properties for an example of a nonpolar vapor, benzene, and for an example of a polar vapor, water, which is able to undergo intermolecular hydrogen bonding. Since adsorption and capillary-condensation processes depend very greatly on the porous structure of the active carbons [8, 14], it was of fundamental importance to compare the sorption properties of carbons differing in the nature of their surfaces but identical in porous structure. This extremely complex experimental problem can, of course, be solved only within a certain approximation.

The surface of an active carbon prepared at a high temperature in absence of an oxidizing atmosphere and brought after cooling into contact with atmospheric oxygen contains oxygen atoms taken up by activated adsorption, which, according to Shilov, form surface oxides of a basic character [1]. For us the details of the structure of these oxides are not of great importance, the only important fact being the presence of chemically bound oxygen atoms on the surface of the carbon, which may be regarded as forming surface oxides that do not give the carbon the power to adsorb inorganic bases (NaOH) from aqueous solution.

Oxidation of the carbon with atmospheric oxygen at 450° results in the formation of surface oxides, which, in the hydrated form, can be regarded as surface carboxyl groups. Simultaneously there is appreciable oxidation of the carbon to carbon dioxide, a measure of which is given by the combustion loss of the carbon. This process is a form of activation of the carbon at a comparatively low temperature, and it results in a change in the porous structure of the carbon as in the usual high-temperature activation with oxidizing gases ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ). The resulting oxidized carbon has ion-exchange properties and is able to adsorb alkali from aqueous solution as a result of the exchange of  $\text{H}^+$  of carboxyls for cations, e.g.,  $\text{Na}^+$ .

The oxidized carbon contains both forms of surface oxides, i.e., the Shilov basic type and the acidic type. These have the character of unimolecular films that do not fully cover the surface. This conclusion follows naturally from an analysis of the comparatively low limiting adsorption values of inorganic bases and acids (up to 1.5 mmoles per gram) when the adsorption of these substances is explained on the ion-exchange scheme.

If the surface oxides are regarded as special sites on the surface of the carbon, then they cannot have any great significance in the adsorption of the vapor of a nonpolar substance such as benzene and will not play the part of active surface regions for this process. This conclusion follows from the very nature of the dispersive interaction of molecules of nonpolar substances and the surface of the carbon. Individual atoms of foreign substances such as oxygen, bound by chemical forces, cannot affect the value of the adsorption potential to any appreciable extent. From this we reach the fundamental conclusion that the surface oxides of the carbon are practically without effect on its adsorption properties with respect to benzene vapor.

Identity of structure in two samples of adsorbents is expressed by identity in specific surface and in pore-volume distribution function. When this condition is fulfilled, the volumes of the different kinds of pores are, of

course, equal. Both of the above factors are of determining significance for the adsorption of benzene vapor, the example of a nonpolar substance selected in our investigation. Consequently, identity of the sorption properties of comparable samples of carbons with respect to benzene vapor (coincidence of sorption isotherms) and equality of the volumes of the micro- and transitional pores (which are of significance for sorption equilibrium) form criteria for the identity of porous structure in carbons, even when there are differences in the nature of the surfaces owing to the presence of surface oxides.

With the method adopted for the preparation of comparable samples of carbons we obtained coincidence, to a satisfactory degree of approximation, of the sorption isotherms for benzene vapor and substantial equality in the volumes of micro- and transitional pores for the pairs of adsorbents. It may be considered, therefore, that our problem is in general solved to an acceptable approximation.

Thus, the characteristic differences that we have noted in the sorption and desorption isotherms for water vapor on comparable pairs of active carbons (A1 and A3, A2 and A4, B1 and B3, and B2 and B4) must be attributed to differences in the chemical nature of their surfaces, and not to differences in porous structure.

In the concepts that we have developed concerning the nature of the sorption of water vapor, surface carbon oxides play the part of primary adsorption centers determining the main course of the processes of adsorption and desorption of water vapor [9]. From this point of view the whole of the characteristic difference in the form of the adsorption isotherms for water vapor has its primary cause in the number of oxygen atoms originally taken up per unit of surface by processes of activated adsorption or of chemisorption. The problem of the nature of the sorption of water vapor by active carbons will be examined in greater detail in future communications.

#### SUMMARY

1. Pairs of samples of active carbon were prepared, each pair being such that the two carbons were very close in porous structure but were distinguished by the presence in one of acidic surface oxides; these oxides were absent in the other, which was freed from them by thermal treatment in a vacuum at about 1000°. It was proved that the samples of carbon chosen for comparison were almost identical in porous structure, although differing in the nature of their surfaces.
2. A study was made of the sorptive properties of carbons with respect to a nonpolar substance, benzene. It was shown experimentally that acidic surface oxides have no appreciable effect on the sorptive power of carbon for benzene vapor over a wide range of equilibrium pressures.
3. The sorption and desorption isotherms of water vapor were investigated for carbons containing acidic surface oxides and for the corresponding carbons freed from these oxides. It was found that the surface oxides had a very considerable effect on the sorptive power of carbons for water vapor, the effect being manifested in the sorption and desorption isotherms of the oxidized carbons by a displacement of the curve in the region of low relative pressure.
4. The basic causes for the differences in the adsorption properties of active carbons differing in the chemical nature of their surfaces were examined.

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## REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

### COMMUNICATION 7. REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH SALT SOLUTIONS

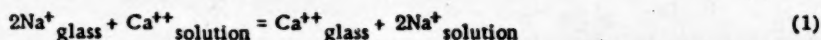
S. K. Dubrovo and Yu. A. Shmidt

In previous communications we have described the interaction of vitreous sodium silicates and aluminosilicates with water and with solutions of acids and alkalis [1-4]. The object of the present work was the determination of the action of solutions of certain salts on these glasses. Such an investigation is of interest because, under the conditions obtaining in practice, the aqueous solutions that act upon glasses and natural minerals will generally contain salts of some kind or other.

Comparatively little study has been devoted to the interaction of glasses with salt solutions. In the course of an investigation into the polishing process, Grebenshchikov [5] studied this problem and noted that the presence of various metal ions in water affects the rate of growth and the physicochemical properties of the siliceous film on the surface of the glass. Schröder [6] studied the attack of solutions of sodium chloride, arsenates, and some other salts on window glass; he found that the destructive effect of caustic soda solutions on glass is intensified by an addition of sodium chloride.

One of the few investigations on the interaction of glasses with solutions of alkaline-earth chlorides is that of Gastev [7], who tried to establish the cause of the increase in the chemical stability of alkali-silicate glasses resulting from an addition of alkaline-earth oxides. With this object he treated glass powders containing 80% by weight of  $\text{SiO}_2$  and 20% by weight of  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$  with calcium chloride, magnesium chloride, and barium chloride solutions. He found that the stability of a sodium silicate glass toward water was increased by treatment of the glass with calcium chloride solution. Magnesium chloride and barium chloride solutions did not have this effect. The author's explanation of this behavior is that only those bivalent ions having a radius close to that of the alkali-metal ion in the glass are adsorbed from solution on the siliceous film formed on the surface. As a result of such adsorption, the protective properties of the film are enhanced.

In Gastev's work there are some errors of principle and method. The author tacitly assumes that the state of the alkaline-earth ions absorbed by the film from the solution is the same as if these ions had been present in the glass from the beginning, being introduced in the process of its preparation. This assumption, however, is incorrect, as can be seen from the following and other considerations. It is known that even small additions of any alkaline-earth oxide to an alkali-silicate glass result in a great increase in the chemical stability of the glass [8, 9]. It follows, however, from Gastev's results that the absorption of barium and magnesium ions has no effect at all on the chemical stability of sodium silicate glass, while the effect of calcium ions is comparatively slight. In determining titrimetrically the amount of alkaline oxides passing from the glass to the solution, the author was unable to take into account that part of the alkali-metal ions (e.g., sodium ions) which are displaced into the solution by calcium ions by the ion-exchange reaction:



and therefore, do not increase the alkali content of the solution. Moreover, the experiments were carried out under conditions that permitted access of carbon dioxide from the air. All these factors, taken together, could seriously distort the results.

We have investigated the interaction of vitreous sodium silicates and aluminosilicates with solutions of sodium, calcium and aluminum chlorides.

# EXPERIMENTAL

Interaction of vitreous sodium silicates and aluminosilicates with sodium chloride solutions. A study was made of the interaction of three sodium silicates and three sodium aluminosilicates with N NaCl at 40°. We have described the experimental procedure previously [1, 3]. The results are given in Tables 1 and 2. As before, the symbols  $\bar{n}_{Na_2O}$ ,  $\bar{n}_{Al_2O_3}$ , and  $\bar{n}_{SiO_2}$  represent the amounts of the respective components that pass into solution from 1 cm<sup>2</sup> of the glass surface. The quantities  $\alpha$  and  $\beta$  are the proportions of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, respectively, passing into solution from the layer of glass that is undergoing interaction.

In the experiments with the silicate Na<sub>2</sub>O · 1.7SiO<sub>2</sub> the presence of sodium chloride in the solution leads to a reduction in the value of  $\bar{n}_{Na_2O}$  and to an increase in the rate of dissolution of the siliceous film. Later, however, when the film is completely dissolved, the value of  $\bar{n}_{SiO_2}$  is found to be less than in the experiments with water. In this case it is probable that, as in the previously described interaction of silicates with alkaline solutions [4], the rate at which the silica of the glass is dissolved now depends on the primary process of the passage of sodium ions into solution, so that with increase in the concentration of sodium chloride this rate diminishes.

The results of the experiments on the interaction of the other sodium silicates with sodium chloride solution confirm our previous conclusions [10], namely that increase in the concentration of sodium chloride in the solution retards the passage of Na<sub>2</sub>O into solution and accelerates the dissolution of the siliceous film. The results that we have obtained for vitreous sodium aluminosilicates point to the same conclusion. In all cases the amounts of alumina passing into solution were very small. At the beginning of the experiments, the presence of sodium chloride in the solution apparently brings about an increase (although this increase is a slight one) in

TABLE 1

Interaction of Vitreous Sodium Silicate of Composition Na<sub>2</sub>O · 1.7SiO<sub>2</sub> with N Sodium Chloride Solution

Solution	Index	Time (hours)					
		1/4	1/2	1	2	4	6
Water	$\bar{n}_{Na_2O} \cdot 10^{-6}$ .....	14	28	51	104	220	352
	$\bar{n}_{SiO_2} \cdot 10^{-6}$ .....	7.2	15	33	140	350	566
	$\alpha$ .....	0.30	0.31	0.38	0.79	0.94	0.97
1 N NaCl	$\bar{n}_{Na_2O} \cdot 10^{-6}$ .....	11	22	45	91	187	259
	$\bar{n}_{SiO_2} \cdot 10^{-6}$ .....	15	35	78	157	319	455
	$\alpha$ .....	0.80	0.96	1.0	1.0	1.0	1.0

TABLE 2

Interaction of Vitreous Sodium Silicates and Aluminosilicates with N Sodium Chloride Solution

Composition	Na <sub>2</sub> O · 2SiO <sub>2</sub>				Na <sub>2</sub> O · 2.3SiO <sub>2</sub>				Na <sub>2</sub> O · 3SiO <sub>2</sub>			
Solution	water		1 N NaCl		water		1 N NaCl		water		1 N NaCl	
Index	time (hours)											
	1	6	1	6	1	6	1	6	1	6	1	6
$\bar{n}_{Na_2O} \cdot 10^{-6}$	19	63	8.2	48	9.1	32	2.9	13	1.6	4.7	0.94	2.5
$\bar{n}_{SiO_2} \cdot 10^{-6}$	3.1	9.3	5.6	77	0.24	1.0	1.0	5.0	0.04	0.08	0.05	0.13
$\alpha$	0.08	0.08	0.37	0.80	0.011	0.014	0.16	0.17	0.008	0.006	0.019	0.017
Composition	Na <sub>2</sub> O · 0.05Al <sub>2</sub> O <sub>3</sub> · 1.7SiO <sub>2</sub>				Na <sub>2</sub> O · 0.05Al <sub>2</sub> O <sub>3</sub> · 2SiO <sub>2</sub>				Na <sub>2</sub> O · 0.15Al <sub>2</sub> O <sub>3</sub> · 1.7SiO <sub>2</sub>			
Solution	water		1 N NaCl		water		1 N NaCl		water		1 N NaCl	
Index	time (hours)											
	1	6	1	6	1	6	1	6	1	6	1	6
$\bar{n}_{Na_2O} \cdot 10^{-6}$	17	50	6.0	28	8.0	22	3.1	10	2.7	6.3	1.5	4.2
$\bar{n}_{Al_2O_3} \cdot 10^{-6}$	0.010	0.13	0.017	0.043	0.003	0.002	0.005	0.011	—	—	—	—
$\bar{n}_{SiO_2} \cdot 10^{-6}$	2.2	6.6	2.8	21	0.22	1.2	0.44	1.6	—	—	—	—
$\alpha$	0.076	0.078	0.27	0.44	0.014	0.027	0.071	0.080	—	—	—	—
$\beta$	0.012	0.052	0.057	0.031	0.008	0.018	0.032	0.022	—	—	—	—



the amounts of alumina passing into solution, but these amounts are later less than in the experiments with water. As we have shown previously [3], in the interaction of sodium aluminosilicates with water, part of the aluminum ions are adsorbed by the residual film from the solution. An analogous phenomenon is observed also in experiments with sodium chloride solution. In experiments with water it was found that the amount of adsorbed aluminum ions is greater when the original glass is less stable, i.e., when the structure of the residual surface film is more open. Correspondingly, the enhanced breakdown of the residual film resulting from the action of sodium chloride solution — which will probably make the structure of the film more open — will facilitate the adsorption of aluminum ions on the surface. This is probably the explanation of the fact that in the experiments with sodium chloride solution the value of  $\beta$  does not increase with time, but diminishes.

The presence of sodium chloride in the solution increases also the rate of dissolution of quartz glass in caustic alkalis. Thus, whereas for the action of a solution containing only caustic soda the value of  $\bar{n}_{\text{SiO}_2}$  for 1 hour is  $0.9 \cdot 10^{-8}$  mole/cm<sup>2</sup> in a 0.01 N solution and  $2.4 \cdot 10^{-8}$  mole/cm<sup>2</sup> in a 0.1 N solution, in a solution containing also sodium chloride at normal concentration the corresponding values of  $\bar{n}_{\text{SiO}_2}$  are  $1.4 \cdot 10^{-8}$  and  $2.9 \cdot 10^{-8}$  mole/cm<sup>2</sup>. Hence, increases in the concentrations of alkali and sodium chloride have the same effect on the rate of dissolution of quartz glass as on the rate of dissolution of the siliceous films on the surface of vitreous sodium silicates and aluminosilicates. As we have already indicated [4], on the surface of quartz glass there may be Si-OH groups, which are capable of participating in ion exchange. It is possible that a similar type of exchange adsorption of sodium ions at the surface may have the same role for quartz glass as that played for other glasses by increase in the concentration of sodium ions in the layer of the siliceous film at the interface with the solution.

TABLE 3

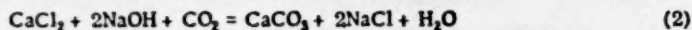
Interaction of Vitreous Sodium Silicates with Calcium Chloride Solutions

Composition	Solution	Index	Time (hours)				
			1/2	1	2	4	6
Na <sub>2</sub> O · 2SiO <sub>2</sub>	Water	$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$	11	18	30	47	62
		$\bar{n}_{\text{SiO}_2} \cdot 10^{-6}$	2.3	3.2	4.2	5.8	9.3
	0.01 N CaCl <sub>2</sub>	$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$ (c)	9.2	14	24	41	52
		$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$ (t)	9.4	14	26	29	34
		$\bar{n}_{\text{SiO}_2} \cdot 10^{-6}$	0.15	0.22	0.46	0.59	0.74
	0.1 N CaCl <sub>2</sub>	$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$ (c)	8.1	14	22	36	46
		$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$ (t)	8.4	14	20	26	30
		$\bar{n}_{\text{SiO}_2} \cdot 10^{-6}$	0.07	0.13	0.19	0.24	0.32
	0.2 N CaCl <sub>2</sub>	$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$ (c)	8.5	14	26	39	47
		$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$ (t)	8.1	14	25	37	41
		$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$ (t without CO <sub>2</sub> )	7.9	13	22	28	—
		$\bar{n}_{\text{SiO}_2} \cdot 10^{-6}$	0.07	0.21	—	0.22	0.30
Na <sub>2</sub> O · 2.3SiO <sub>2</sub>	Water	$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$	5.1	9.1	15	25	32
		$\bar{n}_{\text{SiO}_2} \cdot 10^{-6}$	0.12	0.24	0.54	0.83	1.0
	0.1 N CaCl <sub>2</sub>	$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$ (c)	4.4	7.4	11	18	24
		$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$ (t)	4.5	7.2	11	11	9
Na <sub>2</sub> O · 3SiO <sub>2</sub>	Water	$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$	—	1.6	2.5	3.6	4.7
		$\bar{n}_{\text{SiO}_2} \cdot 10^{-6}$	—	0.040	0.046	0.065	0.078
	0.1 N CaCl <sub>2</sub>	$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$ (c)	—	1.3	2.0	3.1	3.9
		$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$ (t)	—	1.1	0.6	0.4	—
		$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$ (t without CO <sub>2</sub> )	—	0.033	0.025	0.024	0.024
		$\bar{n}_{\text{SiO}_2} \cdot 10^{-6}$	—	0.033	0.025	0.024	0.024

Note: (c) indicates values of  $\bar{n}_{\text{Na}_2\text{O}}$  obtained colorimetrically; (t) indicates titration in presence of CO<sub>2</sub> of the air; (t without CO<sub>2</sub>) indicates titration in absence of CO<sub>2</sub>.

Interaction of vitreous sodium silicates with calcium chloride solutions. The interaction of four sodium silicates with calcium chloride solutions was studied. The experiments were carried out at 40°. In most of the experiments the concentration of calcium chloride was 0.1 N, but for sodium disilicate experiments were carried out also with 0.01 and 0.2 N solutions. The calcium chloride solutions were prepared by the dilution of a stock 5 N solution of calcium chloride to the required concentration with distilled water, which was previously boiled in a silver beaker to remove CO<sub>2</sub> and then cooled rapidly. As our main means for the determination of Na<sub>2</sub>O in solution we selected a colorimetric method, which gives the total amount of sodium in the solution. We also titrated the solution. The results of the experiments are given in Table 3. In the experiments with the silicate Na<sub>2</sub>O · 1.7SiO<sub>2</sub>, spongy growths formed on the surface of the sample; on the outside of these there were white flocks (apparently CaCO<sub>3</sub>), and underneath there were semitransparent formations containing silica. The results of these experiments are, therefore, not comparable with those of the other experiments.

In the experiments with vitreous sodium disilicate the presence of calcium chloride in the solution reduced the values of  $\bar{n}_{\text{Na}_2\text{O}}$  to approximately the same extent as the corresponding concentrations (0.01 and 0.1 N) of sodium chloride did [10]. At the beginning of the experiment (in the first 1-2 hours) the amounts of Na<sub>2</sub>O found in the solution by the two methods coincided within the limits of experimental error. After two hours the amounts of Na<sub>2</sub>O determined colorimetrically were appreciably higher than those found by titration. At about the same time a white substance made its appearance on the surface of the solution. This substance was found to be calcium carbonate, the formation of which by the reaction



led to the removal from the solution of part of the alkali that had passed into it and so to the difference between the values of  $\bar{n}_{\text{Na}_2\text{O}}$  found by titration and the values determined colorimetrically.

In order to avoid absorption of CO<sub>2</sub> from the air in the experiments with 0.2 N CaCl<sub>2</sub>, the beaker containing the solution was closed with a silver cover provided with hydraulic seals for a stirrer and two tubes. Tests were taken through one of the tubes, and through the other air freed from CO<sub>2</sub> was passed over the surface of the solution. The previously prepared solution was boiled in a silver beaker to remove carbon dioxide, brought to the original volume (by weighing), and cooled with the cover in position without access of carbon dioxide. When this procedure was adopted, the discrepancies between the values of  $\bar{n}_{\text{Na}_2\text{O}}$  obtained colorimetrically and by titration were within the limits of experimental error. The somewhat lower values obtained by the titration method at the end of the experiment may indicate slight absorption of calcium ions by the siliceous film in accordance with the reaction (1). In any case, in order of magnitude this absorption is not greater than  $3 \cdot 10^{-6}$  mole/cm<sup>2</sup>. The amount of silicic acid found in the solution was considerably less in the experiments with calcium chloride solutions than in the experiments with water. As in previous work, control experiments were made on the determination of silicic acid in solution after it had been converted into a molecularly dispersed state. The results of these determinations give us reason to consider that the greater part, if not all, of the silicic acid is present in solution in a molecularly dispersed state.

In the interaction of the silicates Na<sub>2</sub>O · 2.3SiO<sub>2</sub> and Na<sub>2</sub>O · 3SiO<sub>2</sub> with calcium chloride solutions, the values of  $\bar{n}_{\text{Na}_2\text{O}}$  were again found to be lower than in the experiments with water. During the first two hours of the experiments with Na<sub>2</sub>O · 2.3SiO<sub>2</sub> the amount of Na<sub>2</sub>O found in the solution by titration was almost identical with the amount found colorimetrically, indicating that in this case the amount of CaO absorbed did not exceed  $2 \cdot 10^{-7}$  mole/cm<sup>2</sup>. Later, however, the values of  $\bar{n}_{\text{Na}_2\text{O}}$  found by titration not only did not increase, but even began to diminish. For both silicates the amounts of silicic acid found in solution in parallel experiments varied greatly (by as much as + 30% from the mean value). Also, toward the end of the experiment  $\bar{n}_{\text{SiO}_2}$  even began to fall in value.

Microscopic investigation of the scum formed on the surface of the solution during the experiments showed that it consisted of crystals of two modifications of calcium carbonate — calcite (large rhombic crystals having a refractive index of 1.658) and aragonite. Exactly similar crystals were formed on the surface of a solution of calcium chloride to which alkali had been added, when this was kept under conditions analogous to those of the experiments. Spectrum analysis of the scum showed that it contained only traces of silicic acid. Crystals of calcite were detected also on the surface of samples of the investigated silicates after experiments conducted in presence of atmospheric carbon dioxide. After treatment of a silicate of composition Na<sub>2</sub>O · 4SiO<sub>2</sub> — which was investigated also by Gastev [7] — with 0.01 N CaCl<sub>2</sub> for one hour at 60° (the conditions of one of Gastev's experiments), a large number of fine crystals were found on the surface of the sample. When we increased the duration of the experiment to six hours, we obtained fairly large crystals of calcite on the surface of the sample (see figure).

In experiments with sodium disilicate conducted in absence of carbon dioxide, formation of calcium carbonate was not detected. When, however, the sample was taken from the solution and placed under the microscope, the formation of very fine calcite crystals could be detected already after 5-10 minutes. In the course of this time an appreciable amount of scum formed on the surface of the solution.

It will be clear from the results described that the interaction of vitreous sodium silicates with calcium chloride solutions is considerably more complex than the processes occurring when only univalent sodium and hydrogen ions are present in solution. On the basis of the high valency of calcium ions as compared with sodium ions, it might be expected that the former would be vigorously absorbed by the residual film and would, therefore, have a much greater retarding action on the rate at which  $\text{Na}_2\text{O}$  passes into solution. Actually, however, the retarding action of calcium chloride solutions was found to be approximately the same as that of sodium chloride solutions of the corresponding concentrations. Moreover, when the concentration of calcium ions is increased from 0.01 to 0.2 N, their retarding action remains practically unchanged. It may, therefore, be supposed that calcium ions do not penetrate deeply into the siliceous film, but are merely adsorbed on its surface. This view is confirmed by findings reported in the literature, namely, that calcium ions enter a glass surface during electrolysis only with difficulty [11] and that they have practically no effect on the potential of a glass electrode [12]. Nevertheless, the appreciable reduction in the values of  $\frac{n}{a}\text{SiO}_2$ , as compared with the values obtained for water, indicates that small amounts of calcium ions are adsorbed on the surface of the film, thus retarding its dissolution.

TABLE 4

Interaction of Vitreous Sodium Disilicate with Aqueous Solutions Containing Aluminium Salts

Solution	Index	Time (hours)				
		1	2	4	6	8
Water	$\frac{n}{a}\text{Na}_2\text{O} \cdot 10^{-6}$	18	30	47	62	76
	$\frac{n}{a}\text{SiO}_2 \cdot 10^{-6}$	3.2	4.2	5.8	9.3	13
	$\alpha$	0.09	0.07	0.06	0.08	0.09
0.003 N $\text{AlCl}_3$	$\frac{n}{a}\text{Na}_2\text{O} \cdot 10^{-6}$	22	32	49	65	83
	$\frac{n}{a}\text{SiO}_2 \cdot 10^{-6}$	0.71	0.98	1.4	3.4	5.1
	$\alpha$	0.016	0.015	0.015	0.026	0.030
0.01 N HCl	$\frac{n}{a}\text{Na}_2\text{O} \cdot 10^{-6}$	23	40	76	87	102
	$\frac{n}{a}\text{SiO}_2 \cdot 10^{-6}$	0.08	0.20	0.66	2.1	4.6
	$\alpha$	0.002	0.003	0.004	0.012	0.022
0.01 N HCl + 0.003 N $\text{AlCl}_3$	$\frac{n}{a}\text{Na}_2\text{O} \cdot 10^{-6}$	24	5	75	93	115
	$\frac{n}{a}\text{SiO}_2 \cdot 10^{-6}$	0.10	0.11	0.26	0.55	0.72
	$\alpha$	0.002	0.001	0.002	0.003	0.003
0.01 N KOH	$\frac{n}{a}\text{Na}_2\text{O} \cdot 10^{-6}$	4.9	12	28	50	64
	$\frac{n}{a}\text{SiO}_2 \cdot 10^{-6}$	2.7	7.9	40	72	109
	$\alpha$	0.24	0.32	0.70	0.72	0.84
0.01 N KOH + 0.003 N $\text{AlCl}_3$	$\frac{n}{a}\text{Na}_2\text{O} \cdot 10^{-6}$	11	21	32	38	48
	$\frac{n}{a}\text{SiO}_2 \cdot 10^{-6}$	0.74	2.0	3.7	6.2	9.4
	$\alpha$	0.034	0.048	0.057	0.081	0.10

In the interaction of vitreous sodium silicates with calcium chloride solution, several secondary processes may occur which complicate the general picture of the phenomenon, for example, the formation of a precipitate of calcium carbonate. Moreover, in some experiments we observed a reduction in the concentration of silica with time, but we did not succeed in finding the cause of this effect because the concentrations of the solutions were very low. Our results show that precipitation of calcium carbonate from solution could have occurred also in Gastev's work [7]. In work with powders such precipitation could (and apparently did) remain unnoticed, so that the observed effect of increased stability could be overestimated.



**Interaction of Vitreous Sodium Disilicate with Aluminum Chloride Solution.** Experiments were carried out on the interaction of vitreous sodium disilicate with water, 0.01 N HCl, and 0.01 N KOH in presence of aluminum chloride at 40°. The results are given in Table 4. In an acid medium and in water the presence of aluminum chloride in the solution had little effect on the rate at which  $\text{Na}_2\text{O}$  passed into solution. In an alkaline medium the rate at which sodium ions passed from the glass to the solution in presence of aluminum chloride rose at first, and then fell. It is interesting to note that the incorporation of alumina in vitreous sodium silicates lowers the rate at which sodium ions pass from the glass to the solution — this fact has been established in our previous investigations. The mechanism of the action of the aluminum ions present in the solution is thus quite different. This again confirms the conclusion reached above, namely, that it is incorrect to make inferences relating to the part played by ions in the glass from a study of the action of aqueous solutions containing these ions on glass.

As can be seen from Table 4, addition of aluminum chloride to water and to 0.01 N solutions of acid and alkali greatly diminishes the rate at which silica passes from the glass to the solution. In this respect the effect of aluminum chloride is analogous to that of calcium chloride. The process of breakdown of vitreous sodium disilicate by solutions of aluminum salts can be represented as proceeding in two stages. The first stage is the exchange of sodium ions from the glass for hydrogen ions from the solution, so that a siliceous film is formed at the surface. This film, and also, possibly, partially dissolved silica, then interacts with aluminum salts — or, in an alkaline medium, with aluminates — with formation of difficultly soluble colloidal hydrated aluminosilicates at the surface. As is well-known, reactions between silicic acid and solutions of aluminates proceed readily with formation of permutite[13]. When aqueous solutions containing aluminum ions interact with vitreous silicates, it may be expected that analogous aluminosilicates will form at the surface of the glass. As a result of the effects discussed we observe a reduction in the rate of breakdown of sodium disilicate when aluminum salts are introduced into the solution.

#### SUMMARY

1. The interaction of vitreous sodium silicates and aluminosilicates with solutions of sodium, calcium, and aluminum chlorides was studied.
2. It was found that, with increase in the concentration of sodium chloride in the solution, there was a reduction in the rate at which  $\text{Na}_2\text{O}$  passed from the glass into the solution and an increase in the rate at which silicic acid passed into the solution.
3. It was shown that, when vitreous sodium silicates interact with calcium chloride solutions in presence of carbon dioxide, secondary processes occur with the formation of precipitates of calcium carbonate.
4. It was shown that in treatments with calcium chloride and aluminum chloride solutions the breakdown of the silica skeleton of silicate glasses is greatly retarded.

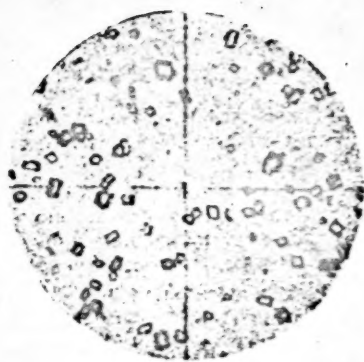
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Calcite crystals on the surface of a vitreous silicate of composition  $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$  treated with calcium chloride solution

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## PHYSICOCHEMICAL STUDY OF LITHIUM PEROXIDE

T. V. Rode, T. A. Dobrynina and G. A. Golder

The possibility of the existence of a lithium peroxide was first suggested by Kralovanszky [1] in 1828. This author considered that when  $\text{LiOH}$  or  $\text{Li}_2\text{CO}_3$  is heated in the air  $\text{Li}_2\text{O}_2$  is formed. In 1857 Trost [2] passed dry oxygen over lithium heated to  $200^\circ$  and obtained a substance containing more oxygen than lithium oxide. This substance decolorized a solution of indigo in hydrochloric acid, was unstable to heat, and reacted at high temperature with gold, silver, and platinum. Trost [2] used iron crucibles in his work. De Forcrand [3] states that the combustion of lithium in oxygen yields only traces of lithium peroxide, since the latter is unstable at the combustion temperature of lithium and decomposes into lithium oxide and oxygen.

Attempts by other authors [4, 5] to prepare lithium peroxide at an oxygen pressure of 100 atm from lithium hydroxide [4] and from lithium oxide [5] at temperatures ranging from  $875^\circ$  to  $570^\circ$  were not successful. The attempts failed because the temperatures used were too high. In a previous paper [6] we have shown, and in the present investigation we have confirmed, that at atmospheric pressure decomposition of lithium peroxide occurs over the range  $285\text{--}315^\circ$ .

Another method for the preparation of alkali-metal peroxides, consisting in the oxidation of solutions of the metals in ammonia at low temperature, did not give satisfactory results in the case of lithium.

Pierron [7] studied the effects of concentration, temperature, and rate of passage of oxygen on the oxidation of a solution of lithium in liquid ammonia. A mixture of lithium oxide and lithium peroxide was always obtained, and the maximum yield of  $\text{Li}_2\text{O}_2$  did not exceed 23%.

The principal method for the preparation of lithium peroxide consists in the oxidation of aqueous-alcoholic solutions of lithium hydroxide with hydrogen peroxide. This method was first proposed by de Forcrand. By the action of a large excess of  $\text{H}_2\text{O}_2$  on an aqueous-alcoholic solution of lithium hydroxide, de Forcrand obtained the compound  $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ , and after dehydration in a vacuum over phosphoric oxide at room temperature for 28 days this yielded almost anhydrous lithium peroxide ( $\text{Li}_2\text{O}_2 \cdot 0.15\text{H}_2\text{O}$ ). Pierron [7] modified de Forcrand's method by raising the precipitation temperature to the boiling point and using 95% ethanol to dissolve the lithium hydroxide. The precipitate obtained was washed with boiling alcohol and vacuum-dried over phosphoric oxide, when it was found to have the composition  $\text{Li}_2\text{O}_2 \cdot 0.01\text{Li}_2\text{O}$ . Cohen [8] treated lithium ethoxide with hydrogen peroxide in an atmosphere of dry helium and obtained the compound  $\text{LiOOH} \cdot \text{H}_2\text{O}$  (or  $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ ), which yielded anhydrous lithium peroxide after being vacuum-dried over phosphoric oxide for 18 days.

In the patent literature a number of methods are given for the preparation of lithium peroxide in presence of various organic substances that facilitate the dehydration of the products [9] or the oxidation of the alkali-metal ethoxide [10-13]. In 1951 Thompson and Kleinberg [14-15] studied the absorption spectrum of a preparation and showed that it is analogous to the absorption spectra of the higher peroxides of sodium and potassium. On the basis of these results the authors [14] postulate the existence of the higher peroxide of lithium  $\text{LiO}_2$ , stable at  $-78^\circ$ .

The properties of lithium peroxide have received little study. In 1932 Blumenthal [16] investigated the thermal dissociation of  $\text{Li}_2\text{O}_2$  by the dynamic method. According to this author's results, a dissociation pressure of 790 mm is already reached at  $198^\circ$ . We, however, have shown that  $\text{Li}_2\text{O}_2$  begins to lose oxygen only at  $285\text{--}315^\circ$  [6]. According to Blumenthal's results [16], the heat of dissociation of  $\text{Li}_2\text{O}_2$  to  $\text{Li}_2\text{O} + \frac{1}{2}\text{O}_2$  is 13.6 kcal; the heat of formation of the peroxide from its elements is 144.8 kcal [17, 18]. In 1953 Rode and Dobrynina [6], working on the thermal analysis of lithium peroxide, established the existence of two modifications of lithium peroxide:  $\alpha\text{-Li}_2\text{O}_2$ , stable up to  $225^\circ$ , and  $\beta\text{-Li}_2\text{O}_2$ , stable up to  $300\text{--}315^\circ$ , above which temperature the  $\beta$ -modification of lithium peroxide decomposes to the oxide. In the same work it was established that the lithium oxide formed by the decomposition does not react with stainless steel, but reacts with the glass of the vessel at  $495^\circ$ .

The crystal structure of lithium peroxide has been investigated by several authors [8, 9, 20, 21]. In the earliest X-ray investigations [8, 19, 20],  $\text{Li}_2\text{O}_2$  crystals were assigned tetragonal symmetry with cell dimensions of  $a = 5.48 \text{ \AA}$ ,  $c = 7.74 \text{ \AA}$ , and  $a/c = 0.708$ . These values, however, led to considerable discrepancies between

the measured and calculated values of the density ( $\sigma_{\text{meas.}} = 2.297 \text{ g/cc}$ ,  $\sigma_{\text{calc.}} = 2.56 \text{ g/cc}$ ) and the assignment of indices to the diffraction lines was found to be ambiguous. In a recent paper by Fehér and coworkers [21], a hexagonal cell is assigned to lithium peroxide, its parameters being  $a = 6.305 \text{ \AA}$ ,  $c = 7.710 \text{ \AA}$ , and  $a/c = 0.8197$ . From these cell dimensions and the measured density the authors calculated the number of atoms in the elementary cell to be  $z = 8$ . The calculated value of the density was  $\sigma = 2.48 \text{ g/cc}$ . Optical investigations by these authors [21] showed the presence of an axis of symmetry of the sixth order in lithium peroxide crystals. Below, we give our results on the X-ray investigation of the  $\alpha$ - and  $\beta$ -modifications of lithium peroxide; they confirm the results obtained by Fehér and coworkers [21] for the  $\alpha$ -modification.

## EXPERIMENTAL

### Experimental Procedure

We carried out a physicochemical study of the system consisting of lithium peroxide and lithium oxide, using various methods of physicochemical analysis: in addition to investigation of composition-temperature curves under dynamic conditions on a torsion balance and chemical and X-ray analysis of the starting materials, intermediate products, and final products formed by heat, we carried out a precise thermographic investigation coupled with parallel determinations of the amount of oxygen evolved. As a result of this complex study we obtained the composition-temperature diagram for the system  $\text{Li}_2\text{O}_2\text{--Li}_2\text{O}$ .

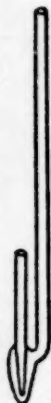


Fig. 1. Vessel for determining the thermogram with simultaneous measurement of evolved gas.

The thermograms were recorded on a Kurnakov photo-registering pyrometer, which is described in detail in a book by Berg, Nikolaev and Rode [22]. Heating was carried out in accordance with a straight-line law in a crucible furnace, which was connected to the mains through a voltage regulator. Heating was at the rate of  $6^\circ$  per minute. Two thermograms were recorded at a rate of  $100^\circ$  per minute by the method proposed by Berg and Rassonskaya [23]. Accuracy in the thermographic recording was attained by considerably reducing the amount taken, which was from 0.07 to 0.2 g.

Thermograms were determined in silica test tubes, in stainless steel beakers, and also in Pyrex Stepanov vessels [22], which we modified slightly (see Fig. 1). In all experiments the test samples were taken in a chamber containing air freed from moisture and carbon dioxide by suitable absorbents ( $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O}_2$  and  $\text{KO}_2$ ). The exit tubes of the Stepanov vessels were connected via a sulfuric acid absorber to a measuring buret, by means of which the kinetics of oxygen evolution could be followed during the recording of the thermogram, so that polytherms for the decomposition of the investigated samples could be obtained. The gas was brought to normal conditions, and a correction was made for its thermal expansion. In experiments carried out in Stepanov vessels, the specimens were again isolated from moisture and atmospheric carbon dioxide during the heating process.

In order to interpret the thermal effects observed on the thermograms, separate experiments were carried out in which specimens were heated to temperatures below and above those of the thermal effects. These specimens were investigated by X-ray and chemical analysis, and for control purposes their thermographs were determined. The chemical analysis was for active oxygen, which was determined from the volume of gas evolved in the catalytic decomposition of the specimens with cobalt sulfate solution.

For X-ray analysis the specimens were placed in Pyrex capillaries in the dry chamber referred to above. Copper radiation with a nickel filter was used in a RKU-114 camera. The spacing of the interference lines was measured with an IZA-2 comparator having a modified optical system, the magnification being about 4.

Composition-temperature range curves were determined under dynamic conditions from the loss in weight of the substance, which was measured on a torsion balance. Weighing was performed without removing the specimens from the vertical tube furnace, so as not to disturb the course of the heating of the substance. Readings were taken every minute. Heating was carried out both in an atmosphere of dry air and in a stream of dry oxygen, the rate of heating being 13, 5.5, and 1.5 degrees per minute. The lithium peroxide was synthesized by Dobrynina and had the following composition: lithium peroxide - 98.93%; total impurity ( $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ ) - 1.07%;  $\text{CO}_2$  - none detected.



### Thermographic Investigation

Fig. 2 shows the differential thermogram for lithium peroxide (Curve 1) and the simultaneous record (polytherm) of the amount of oxygen evolved during heating (Curve 2). Along the axis of abscissas time is plotted in minutes for both curves. The data for Curve 2 are given in Table 1.

The differential thermogram (Curve 1, Fig. 2) shows the presence of the following thermal effects: at the beginning, at about 100°, there is scarcely appreciable inflection corresponding to the removal of loosely bound water; then, from 225° to 235°, there is a well-marked irreversible exothermic effect. Chemical analysis of a specimen heated — also in a Stepanov vessel — to 250°, i.e., above the temperature for the effect, showed that this effect is not accompanied by change in the composition of the substance. This can be seen also from Curve 2 (Fig. 2) for the evolution of oxygen, for in the section corresponding to this exothermic effect no evolution of gas has yet occurred. The irreversibility of this effect was established by an examination of the curves (not given here)

TABLE 1

Evolution of Gas During the Heating of Lithium Peroxide

Time (minutes)	Temperature (°C)	Volume of gas evolved (ml at STP)	Reading of differential galvanometer (scale divisions)	Time (minutes)	Temperature (°C)	Volume of gas evolved (ml at STP)	Reading of differential galvanometer (scale divisions)
0	18	0	0	47	342	33.5	-5.0
15	145	0	-0.5	48	—	41	-5.0
25	210	0.0	-0.7	49	—	47.2	-4.5
37	295	0.5	-0.7	50	367	50.2	-2.5
39	—	1.6	-0.8	51	375	51.4	-0.3
41	315	5.0	-1.3	58	—	51.4	+1.0
42	—	7.8	-1.5	65	437	52.4	+2.0
43	325	9	—	82	—	53.4	+4.7
44	—	11	-2.7	103	580	54.5	+4.5
45	—	18.5	-3.5	115	—	54.5	+4.0
46	—	26	-4.5	130	723	54.5	+4.5

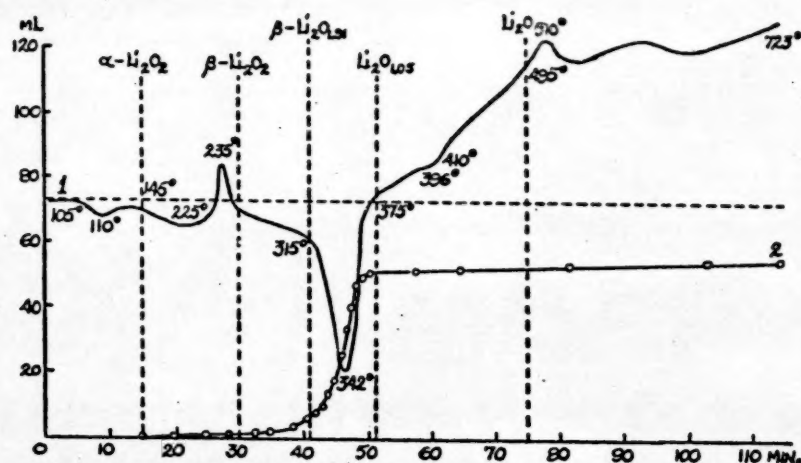


Fig. 2. Thermogram for lithium peroxide, with simultaneous record of the decomposition polytherm.

for the cooling of preparations heated to 250° and for the reheating of the same preparations. The irreversibility of the process and the constancy of composition gave reason to suppose that this exothermic effect is associated with a polymorphous transformation of lithium peroxide. As will be seen below, X-ray analysis confirmed the correctness of our supposition regarding the nature of this effect and the existence, therefore, of lithium peroxide in two modifications. The first of these, which is obtained under the usual conditions of synthesis and is stable up to 225°, we have called  $\alpha$ -Li<sub>2</sub>O<sub>2</sub> [6], and the second, which is formed as the result of changes occurring at 225° and is stable up to 285-315°, we have called  $\beta$ -Li<sub>2</sub>O<sub>2</sub>.

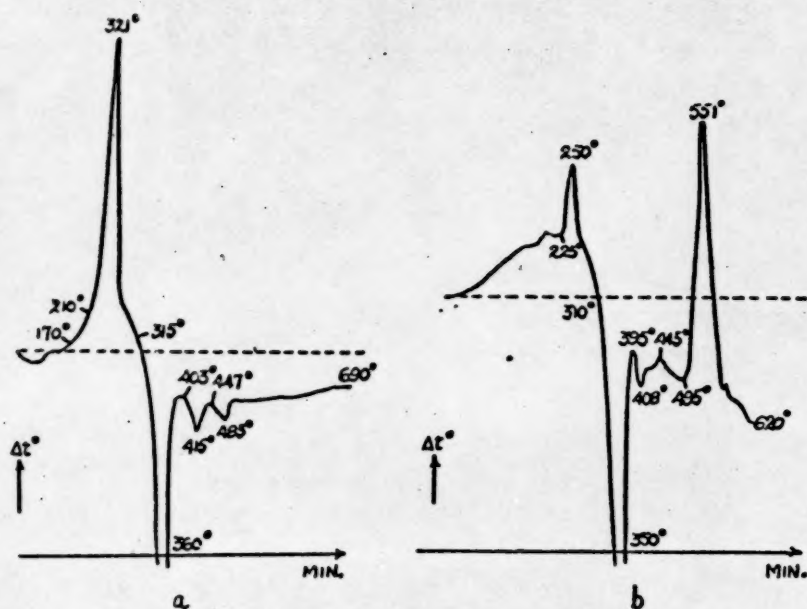


Fig. 3. Thermogram for lithium peroxide determined in a steel vessel without exclusion of moisture and atmospheric carbon dioxide: a) resistance 300 ohms; b) resistance 100 ohms\*

Further along the thermogram (Fig. 2) there is a very large endothermic effect beginning at 315°, which is accompanied by vigorous evolution of oxygen and so corresponds to the decomposition of the  $\beta$ -modification of lithium peroxide. The decomposition polytherm for Li<sub>2</sub>O<sub>2</sub> (Curve 2, Fig. 2, and Table 1) has a sharp rise associated with vigorous evolution of oxygen exactly in the region of this endothermic effect. The chemical analysis of a preparation that had been heated in a Stepanov vessel to 315° showed that it corresponded in composition to Li<sub>2</sub>O<sub>1.91</sub>. This indicates that slow decomposition of the  $\beta$ -modification of Li<sub>2</sub>O<sub>2</sub> begins somewhat below 315°. This is shown also by an examination of the decomposition polytherm for lithium peroxide (Curve 2, Fig. 2, and Table 1). Chemical analysis of a preparation that had been heated with exclusion of moisture and atmospheric carbon dioxide to 375° showed that it corresponded in composition to Li<sub>2</sub>O<sub>1.95</sub>, which again confirms the correctness of our explanation of the effect as due to the decomposition of the  $\beta$ -modification of lithium peroxide. However, the decomposition product is not pure lithium oxide, but is a preparation containing a slight excess of active oxygen (Li<sub>2</sub>O<sub>1.95</sub>).

Finally, at 495-510° there is a small but clearly marked exothermic effect on the thermogram, which might possibly be explained by the crystallization of amorphous lithium oxide formed in the decomposition. However, the X-radiogram of a preparation obtained by treatment in absence of moisture and atmospheric carbon dioxide at 375°, i.e., immediately above the temperature of the decomposition effect, showed that lithium oxide is formed directly in the crystalline state (see below in the section on X-ray studies; see also Table 4). Further investigation showed that this exothermic effect corresponded to interaction with the glass of the vessel. In order to exclude the

\* This description of the curves does not appear to be correct. See text. [Publisher].

possibility of such interaction we determined the thermogram in a 0.5 ml stainless steel beaker, and the curve obtained is given in Fig. 3a. On this curve there are again some well-defined effects: an exothermic effect corresponding to the conversion of the  $\alpha$ -modification of lithium peroxide into the  $\beta$ -modification, which begins here at 210°, and an endothermic effect corresponding to the decomposition of the  $\beta$ -modification of lithium peroxide, which begins at 315°. Beyond this point there is no exothermic effect to be found on the thermogram. The disappearance of the exothermic effect at 495-510° on the thermogram when Pyrex glass is replaced by stainless steel confirms that this exothermic effect corresponds with the interaction of lithium oxide formed by decomposition of the peroxide with the glass of the vessel. This is confirmed also by a thermogram determined in a quartz-glass test tube (Fig. 3b), the conditions then being such that the interaction of lithium oxide with the glass will be even greater. On this thermogram the exothermic effect for the interaction of the lithium oxide formed with silica, which begins at 495°, is even more marked than in the experiments in a Pyrex-glass vessel.

Kracek [24] has studied the phase diagram for the binary system lithium oxide-silica, and he established the existence of three intermediate compounds in this system:  $2\text{Li}_2\text{O} \cdot \text{SiO}_2$ ,  $\text{Li}_2\text{O} \cdot \text{SiO}_2$ , and  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ . Austin [25] gives X-ray data for all these three compounds. The chemical analysis of the preparation that we obtained in a quartz vessel heated to 658° and a comparison of its X-radiogram with the X-radiograms given by Austin [25] (see below, Table 5) completely confirm the results of thermographic and chemical analysis, namely, that the lithium oxide formed reacts with the glass of the vessel at about 500° with formation of lithium monosilicate  $\text{Li}_2\text{O} \cdot \text{SiO}_2$  ( $\text{Li}_2\text{SiO}_3$ ).

On the thermograms determined in steel beakers and quartz test tubes (Fig. 3a and 3b), i.e., under conditions such that the specimens were not isolated from the action of atmospheric moisture, we observed two additional small endothermic effects beginning at about 400° and at about 445°, respectively; these were due to the action of atmospheric moisture and the formation of a small amount of lithium hydroxide.

It is reported in the literature [17, 18] that lithium peroxide is not hygroscopic, but this is not true. Our observations have shown that, when allowed to stand in a desiccator over dilute (2%) sulfuric acid, both the  $\alpha$ - and  $\beta$ -modifications of lithium peroxide avidly absorb moisture with formation of lithium hydroxide. Both of the additional effects referred to above - at 403-415° and at 445° - correspond to the presence of lithium hydroxide, which undergoes a polymorphous change when the first effect occurs, as established in the work of Khitrov, Khitrova and Khmelkov [26], and melts without decomposition when the second effect occurs.

The hypothesis that we advanced in a previous paper [6] regarding the cause of the first of these additional effects (at 403-415°) (removal of water in excess of that required by the formula  $\text{LiOH}$ ) has not been confirmed. This effect is analogous to the effect given by sodium hydroxide and is to be explained by the occurrence of a polymorphous change of lithium oxide.

On a thermogram for  $\text{Li}_2\text{O}_2$  determined in a vacuum with continuous removal of the oxygen evolved by pumping, the endothermic effect for the decomposition of the  $\beta$ -modification of  $\text{Li}_2\text{O}_2$  began at 283°. The rate of heating, which also has an effect on the decomposition temperature, was the same in both cases, namely, 6 degrees per minute. It follows, therefore, that with reduction of pressure the decomposition temperature of  $\beta$ - $\text{Li}_2\text{O}_2$  falls.

On thermograms determined at 100 degrees per minute, which are not given here, the beginning of the endothermic decomposition effect was at 390°.

#### Curves for the Loss in Weight. Determined on a Torsion Balance

Fig. 4 shows curves for the dependence of the loss in weight, as determined with a torsion balance, on time, and Fig. 5 shows curves for its dependence on temperature. An examination of the curves in Figs. 4 and 5 shows that increase in the rate of heating raises the temperature at which decomposition of  $\beta$ - $\text{Li}_2\text{O}_2$  begins: at 13 degrees per minute (Curve 1) decomposition began at about 310°; at 5.5 degrees per minute (Curve 2) it began at 288°; and at 1.6 degrees per minute (Curve 3) it began at 287°. Comparison of the curves given in Fig. 5 shows that increase in the rate of heating displaces the whole of the curve for the loss of weight into the region of higher temperatures.

Two curves determined at 5.5 degrees per minute, one obtained by heating  $\text{Li}_2\text{O}_2$  in an atmosphere of dry air, and the other obtained in a stream of dry oxygen, show that, as might be expected, the presence of oxygen somewhat retards the decomposition of lithium peroxide.



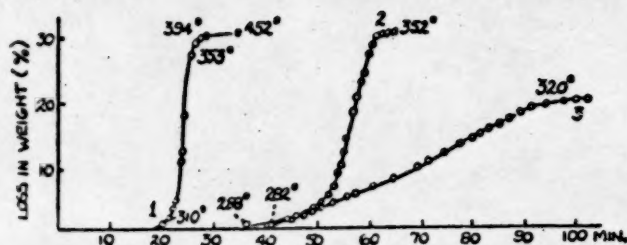


Fig. 4. Curve for the dependence of the loss in weight of lithium peroxide in an atmosphere of air on the rate of heating: 1) 13° per minute, 127 ohms; 2) 5.5° per minute, 100 ohms; 3) 1.6° per minute, 70 ohms.

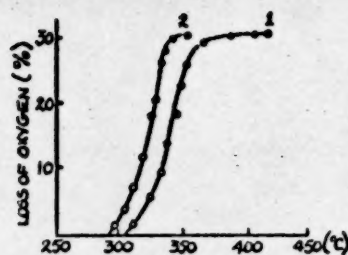


Fig. 5. Curve for the dependence of the loss in weight of lithium peroxide in an atmosphere of air on the rate of heating: 1) 13° per minute; 2) 5.5° per minute.

#### Results of an X-Ray Study of Preparations Obtained by Heating Lithium Peroxide

In recent work by Feher and coworkers [21] it was established that lithium peroxide synthesized in the usual way has hexagonal symmetry with cell parameters of  $a = 6.305$  Å,  $c = 7.710$  Å, and  $a/c = 0.8197$  Å. Table 2 gives our results on the interplanar spacing of the  $\alpha$ -modification of lithium peroxide. The data of Feher and coworkers [21] is given in the same table for comparison, and they agree very well with ours. All of the observed lines can be assigned to indices of the hexagonal lattice. Our results, therefore, confirm those of Feher [21] and show that the  $\alpha$ -modification has hexagonal symmetry with the cell parameters given above; they conflict with the results of previous authors [8, 9, 20], which assign a tetragonal cell to this substance.

TABLE 2

Interplanar Spacing of  $\alpha$ -Li<sub>2</sub>O<sub>2</sub>

No.	Our results		Feher's results		hkl
	I	d	I	d	
1	weak	3.84	medium	3.86	002
2	strong	2.74	mod. strong	2.74	020
3	v. strong	2.59	v. strong	2.59	021
4	mod. strong	2.23	medium	2.23	022
5	v. weak	1.90	v. weak	1.94	004
6	medium	1.87	medium	1.88	023
7	v. strong	1.58	strong	1.58	220
8	weak	1.45	weak	1.46	222
9	strong	1.34	mod. strong	1.34	223
10	weak	1.29	weak	1.29	042
11	weak	1.22	weak	1.21	043
12	medium	1.02	medium	1.02	045
13	medium	1.00	medium	0.993	226

TABLE 3

Interplanar Spacing of  $\beta$ -Li<sub>2</sub>O<sub>2</sub>

No.	I	d	No.	I	d
1	medium	4.35	6	weak	1.86
2	medium	3.08	7	medium	1.76
3	v. strong	2.75	8	strong	1.66
4	medium	2.52	9	medium	1.49
5	v. weak	1.94			

The  $\beta$ -modification of lithium peroxide, the existence of which had been established by the method of thermography, was synthesized in a separate experiment from the  $\alpha$ -modification by heating it for six hours at 235° in a current of dry oxygen. Its interplanar spacing is given in Table 3. However, as the crystals of  $\beta$ -Li<sub>2</sub>O<sub>2</sub> evidently belong to a lower symmetry, it was not found possible to carry out the assignment of indices and the calculation of parameters.

It was established by thermography and simultaneous determination of decomposition polytherms that lithium peroxide decomposes at about 300-315° with formation of lithium oxide when the specimen is well-isolated from the action of atmospheric moisture and carbon dioxide. In view of the presence of an exothermic effect at 495° on the Li<sub>2</sub>O<sub>2</sub> thermogram, the question arose of whether this was a crystallization effect of lithium oxide formed in the amorphous state. Hence, in a separate experiment a sample of Li<sub>2</sub>O<sub>2</sub> was heated to 350° with careful exclusion of moisture and carbon dioxide. The X-radiogram of this sample showed that it consisted of crystalline lithium oxide. Its interplanar spacing is given in Table 4. Mensuration of the X-radiogram gave spacings in good agreement with those reported in the literature [27-29] for the cubic lattice of lithium oxide having the parameter  $a = 4.619$  Å.



TABLE 4

Interplanar Spacing of  $\text{Li}_2\text{O}$ 

No.	I	d		hkl
		experimental	calculated	
1	v. strong	2.66	2.664	111
2	weak	2.30	2.305	200
3	v. strong	1.63	1.630	220
4	strong	1.40	1.400	311
5	medium	1.15	1.151	400
6	medium	1.06	1.058	331
7	strong	0.945	0.924	422
8	medium	0.890	0.888	511
9	medium	0.820	0.815	440
10	medium	0.781	0.780	531

TABLE 6

Composition-Temperature Diagram for the System  $\text{Li}_2\text{O}_2-\text{Li}_2\text{O}$  (under conditions of careful exclusion of atmospheric moisture and carbon dioxide)

No.	Temperature (°C)	Composition	X-ray data
1	20	$\alpha-\text{Li}_2\text{O}_2$	Given in Table 5
2	200	$\alpha-\text{Li}_2\text{O}_2$	Identical with preceding
3	215	$\alpha-\text{Li}_2\text{O}_2$	Ditto
4	235	$\beta-\text{Li}_2\text{O}_2$	Given in Table 6
5	315	$\beta-\text{Li}_2\text{O}_{1.91}^*$	
6	350	$\text{Li}_2\text{O}_{1.95}$	Given in Table 7
7	480	$\text{Li}_2\text{O}$	Identical with preceding
8	658	$\text{Li}_2\text{SiO}_3$	Given in Table 8

(heated in a quartz vessel)

\* Observed displacement of interference lines is within limits of experimental error.

Table 5 gives the interplanar spacing of Preparation No. 10. This material was obtained as the result of the determination of a thermogram for temperatures up to 658° in a Stepanov vessel, which was completely destroyed by the end of the experiment. Comparison of the results obtained for this preparation with Austin's results [25], which are given in the same table, confirms the suggestion made above concerning the formation of lithium monosilicate  $\text{Li}_2\text{SiO}_3$  by reaction of lithium oxide with the glass of the vessel at temperatures above 500°.

Composition-Temperature Diagram for the System  $\text{Li}_2\text{O}_2-\text{Li}_2\text{O}$ 

We have also determined the composition-temperature diagram for the system  $\text{Li}_2\text{O}_2-\text{Li}_2\text{O}$ . Weighed samples of lithium peroxide were heated in Stepanov vessels at various temperatures (as indicated by the thermograms) for several hours. At the end of the treatment the loss in weight was determined and chemical and X-ray analyses were carried out on the products. A comparative examination of all of the results so obtained made it possible to construct the composition-temperature diagram of the lithium peroxide-lithium oxide system, and we give this in Fig. 6. The corresponding numerical data are given in Table 6.

The field of existence of the  $\alpha$ -modification of lithium peroxide extends from room temperature to 225°, and it does not decompose at this temperature, but passes into the  $\beta$ -modification, which is stable up to 280°. Up to this temperature, no decomposition of the  $\beta$ -modification of lithium peroxide is observed in an atmosphere free from moisture and carbon dioxide. Between 280° and 315° very slow decomposition of  $\beta-\text{Li}_2\text{O}_2$  sets in and proceeds until a product of composition  $\text{Li}_2\text{O}_{1.91}$  is obtained. At 315° there is vigorous decomposition, but complete loss of active oxygen to give a product having the composition of lithium oxide is not observed, and the decomposition product corresponds to the formula  $\text{Li}_2\text{O}_{1.95}$ . Thus, between the compositions  $\beta-\text{Li}_2\text{O}_2$  and  $\beta-\text{Li}_2\text{O}_{1.91}$  and from  $\text{Li}_2\text{O}_{1.95}$

TABLE 5

Interplanar Spacing of Preparation No. 10, Heated to 658° in a Quartz Stepanov Vessel

No.	Data for Preparation No. 10		Data of Austin for $\text{Li}_2\text{SiO}_3$ [25]	
	I	d	I	d
1	medium	4.71	v. strong	4.70
2	medium	3.98	medium	4.02
3	strong	3.36	medium	3.32
4	v. strong	2.74	v. strong	1.72
5	strong	2.37	medium	2.35
6	weak	1.79	weak	1.78
7	medium	1.65	weak	2.66
8	medium	1.58	medium	1.57

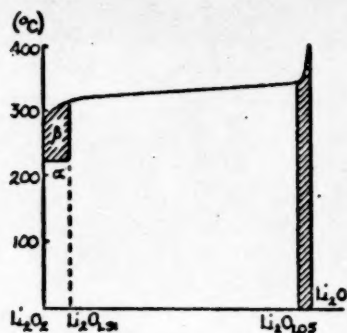


Fig. 6. Composition-temperature diagram for the system lithium peroxide-lithium oxide.

to  $\text{Li}_2\text{O}$ , regions of phases of variable composition are observed, and between the compositions  $\beta\text{-Li}_2\text{O}_{1.91}$  and  $\text{Li}_2\text{O}_{1.88}$  there is a heterogeneous region.

#### SUMMARY

1. A physicochemical study was made of the system  $\text{Li}_2\text{O}_2\text{-Li}_2\text{O}$  with the application of various methods of physicochemical analysis. Composition-temperature curves were determined under dynamic conditions with a torsion balance, chemical and X-ray analyses were made on the original substances and the intermediate and final products formed during heating, and also a precision thermographic investigation was carried out with simultaneous determination of the amount of oxygen evolved.

2. On the basis of the results of this complex study we constructed the composition-temperature diagram for the system lithium peroxide-lithium oxide (Fig. 6).

3. It was established that in this system there is an irreversible polymorphous change at about  $225^\circ$  and that lithium peroxide occurs in two modifications:  $\alpha\text{-Li}_2\text{O}_2$ , stable to  $225^\circ$ , and  $\beta\text{-Li}_2\text{O}_2$ , stable to  $280\text{-}315^\circ$ .

4. The results of Feher and coworkers [21] concerning the assignment of  $\alpha\text{-Li}_2\text{O}_2$  to the hexagonal syngony (and not the tetragonal, as considered previously) were confirmed. The interplanar spacings of the  $\beta$ -modification were reported.

5. It was shown experimentally that lithium peroxide decomposes endothermically over the range  $315\text{-}345^\circ$  (at a rate of heating of  $5.5\text{-}6$  degrees per minute). The beginning of slow decomposition with formation of a product of composition  $\beta\text{-Li}_2\text{O}_{1.91}$  is observed already at  $280\text{-}315^\circ$ .

6. It was shown that, at temperatures of  $495^\circ$  and above, the lithium oxide formed by decomposition reacts exothermically with the glass of the vessel and yields lithium monosilicate. Lithium oxide does not undergo any reaction when heated for a short time with stainless steel at  $690^\circ$ .

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# SYNTHESIS OF 2,2'-AZOBIS[2-METHYLPROPIONITRILE]

## Labeled with Radioactive Carbon ( $C^{14}$ )

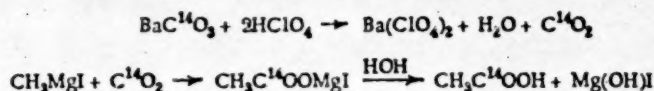
M. M. Koton, T. M. Kiseleva and F. S. Florinsky

Free radicals are now extensively applied in the initiation of polymerization reactions, and for the detailed study of the mechanisms of such reactions initiators containing radioactive carbon in their molecules have been used [1]. Koton, Kiseleva and Bessonov [2] have synthesized benzoyl peroxide containing radioactive carbon ( $C^{14}$ ) in the carbonyl group, and they showed that benzoyl peroxide breaks down into benzoate radicals which initiate the polymerization of styrene. In view of the extensive use of 2,2'-azobis[2-methylpropionitrile] as an initiator in radical polymerization, we have now carried out the synthesis of this compound labeled with radioactive carbon ( $C^{14}$ ).

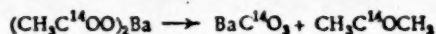
## EXPERIMENTAL

### Preparation of Radioactive Acetone $CH_3C^{14}OCH_3$

Acetic acid containing radioactive carbon in the carboxyl was prepared [3] for use in the synthesis of radioactive acetone:



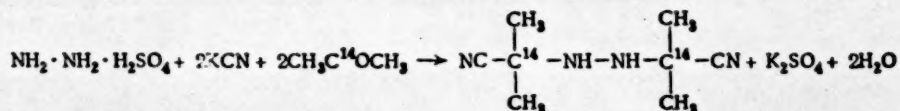
Carbon dioxide was prepared in a special apparatus from 0.25 g of active barium carbonate by the action of 5 ml of perchloric acid. The carbon dioxide was cooled, first with liquid nitrogen, and then with solid carbon dioxide, and 30 ml of 0.8 N ethereal methylmagnesium iodide was added. The reaction mixture was kept for one hour in an ice bath and then for one hour at room temperature for completion of the reaction. Decomposition was effected with 10% aqueous hydrochloric acid, and the ethereal solution was separated, washed, and dried. Ether was distilled off, 2 g of silver sulfate was added to the residue, and acetic acid was distilled over into a titrated solution of barium hydroxide. The resulting solution of barium acetate was evaporated to dryness in a platinum dish. The yield of barium acetate was 0.50 g (78.8%). It was subjected to pyrolysis at 500° [4]:



and radioactive acetone was obtained in quantitative yield.

### Preparation of Radioactive 2,2'-Hydrazobis[2-methylpropionitrile] [5]

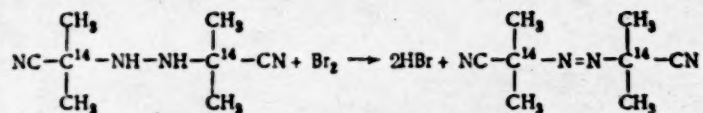
A solution of 12.15 g of hydrazine sulfate in 50 ml of water was warmed slightly, and concentrated potassium cyanide solution (12.15 g of KCN in 15 ml of water) and 10.85 g of radioactive acetone were added. The mixture was stirred vigorously until crystallization set in. After twelve hours the crystals were separated from the liquid, washed with water, and used in the next stage of the synthesis without further purification. The yield was 15.0 g.



### Preparation of Radioactive 2,2'-Azobis[2-methylpropionitrile]

The 2,2'-hydrazobis[2-methylpropionitrile] prepared as above (15.0 g) was dissolved in 50 ml of ethanol, the solution obtained was warmed slightly, and a solution of 15 ml of concentrated hydrochloric acid in 30 ml of

water was added. The solution was cooled with ice and salt, and it was then stirred vigorously while a solution of 4 g of bromine in 415 ml of water was added slowly. The end of the oxidation process was indicated by permanent coloration of the solution. A white crystalline precipitate formed; it was separated, washed with water, and recrystallized from ether or ethanol.



The yield was 6.6 g of substance in the form of fine white crystals, melting with decomposition at 100-103°.

Found %: N 34.05

$\text{C}_8\text{H}_{12}\text{N}_4$  Calculated %: N 34.14

According to the results obtained in S. E. Bresler's laboratory, the specific activity of the preparation obtained was 30 microcuries per gram.

#### SUMMARY

The synthesis is described of 2,2'-azobis[2-methylpropionitrile] labeled with radioactive carbon.

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## PRESENT STATE OF THE CATALYSIS PROBLEM AND THE THEORETICAL BASIS OF THE SEARCH FOR CATALYSTS

A. A. Balandin

(Paper read at a general meeting of the Division of Chemical Sciences  
of the Academy of Sciences of the USSR, March 31, 1955)

In 1954 there was much activity in the field of catalysis. New monographs on catalysis appeared (Boreskov [1], Emmett [2], *Advances in Catalysis* [3], a section in a book by Semenov [4]). In April there was a conference in Moscow on the electronic properties of catalysts, and at this conference important communications were made relating to experimental support for the electronic theory of catalysis (S. Z. Roglinsky, F. F. Volkenshtein) the desorption of molecules under the action of light was described (A. N. Terenin).

In June there was an international conference in Paris on the structure and texture of catalysts [5]. The Soviet delegation was headed by B. A. Kazansky, and papers were read at the conference by G. M. Panchenkov and L. A. Nikolaev. The conference again showed the necessity for the application of modern methods in the study of solid catalysts, namely, X-ray-structure, electronographic, electron-microscopic, magnetic, adsorption, thermographic, calorimetric, and other methods. Several papers were devoted to the electronic theory of catalysis.

In October there was an All-Union conference in Alma Ata on hydrogenation and oxidation (president of organizing committee D. V. Sokolsky) [6]. At the end of October, under the initiative of A. V. Topchiev, a conference was called in Moscow on the complex chemical treatment of natural and industrial petroleum gases, and about one-half of the papers were devoted to applied catalysis. The work of the Moscow Inter-Institute Seminar on Catalysis was renewed.

In 1954 a group of scientists with the cooperation of the most eminent specialists on catalysis in the country worked out a plan for tackling the problem of the "scientific basis of the selection of catalysts", which was listed by the Presidium of the Academy of Sciences of the USSR among problems of particular importance [7]. In connection with the development of the plan, a conference was held in Moscow University, and not only Moscow scientists, but also scientists from Leningrad, the Ukraine, White Russia and the Caucasus took part. An important result of the work done was the isolation of the central problem in catalysis — the selection of catalysts. Other valuable results were the experiment of combining the efforts of various schools of catalysis, the realization that the theory of catalysis in its present state is able to indicate what experimental data are required for the solution of the problem, and the support given to this undertaking by industry. The development of the theory of catalyst selection on the basis of material relating to practically important reactions should result in knowledge enabling us to direct and control these reactions better. Investigations on the problem of the scientific basis of the selection of catalysts have been included in the plans of several institutes, and they have already been started; a scientific council has been organized to deal with this problem, and it has begun work.

During 1954, important results on inorganic and organic catalysis were published. Of the latter the following should be noted: the formation of hydrocarbons having five-membered rings (Kazansky and Liberman [8], Shuikin [9]), hydrogenation (Ponomarev [10], Freidlin [11], Sokolsky [12]), alkylation (Turova-Polyak [13]), isomerization (Levina [14]), reactions of heterocycles (Yuryev [15], Sultanov [16], Kozlov [17]), mechanism of dehydration (Topchieva [18] and others).

The interest in catalysis is understandable, for such important industries as the manufacture of high-quality motor fuels, synthetic rubber, plastics, solvents, ammonia, sulfuric and nitric acids, etc., are based on catalysis. The volume of production in the catalysis industries is very great; thus in 1953, 137 million tons of gasoline valued at 22 billion dollars was manufactured in the U. S. by catalytic cracking [19]. Catalysis and its application are developing rapidly. There can be no doubt that in the future a considerable part of the material requirements of mankind will be satisfied with the aid of the catalytic treatment of coal, petroleum, gases, water and air.



The selection of catalysts has generally been carried out in an empirical fashion. This method is a very slow one; for example, it has now become known that in Germany 20,000 substances were tried as catalysts for the synthesis of ammonia. In foreign countries there are several institutes and large laboratories which work on the selection of catalysts.



Fig. 1. Layers: I) carrier and foreign materials; II) active centers; III) reacting atoms; IV) substituents attached to them; V) molecular-adsorption layer; VI) diffusion layer.

It is necessary to find rational, nonempirical methods for the selection of catalysts. There are various schools and trends in the theory of catalysis: the deformation theory (Zelinsky [20], Bodenstein [21]); the theory of intermediate compounds (Sabatier [22]) and its modern variant, the theory of intermediate chemisorption (Rideal [23], Boreskov [24]); the multiplet theory (Balandin [25]); the theory of nonhomogeneity of surface (Taylor [26], Temkin [27], Roginsky [28]); the theory of assemblages (Kobozov [29]); the theory of supersaturation (Roginsky [30]); the electron-chemical theory (Riginsky and Volkenshtein [31]); the radical-chain theory (Semenov and Voevodsky [4]); the theory of absolute reaction rates (Temkin [32], Eyring [33]). Recently, a drawing together of different points of view is to be noted and several general principles have been elucidated which form the general outline of a unified theory of catalysis based on the theory of the structure of matter. It has been found that different theories often refer to different aspects of the phenomenon and are mutually complementary. This is particularly clear when considered in relation to the ideas developed by the present author [34] concerning the layered structure of the catalytic active complex (Fig. 1). The theories enumerated above relate mainly to layers II and III, whereas the work on hydrogenation by S. V. Lebedev, for example, relates to layer IV, and many of the investigations of S. Yu. Elovich on hydro-

genation relate to layer VI.

We shall now examine the contributions made to the development of the problem of the selection of catalysts by the authors of theories relating to this problem. The chemical theory of intermediate compounds is able to explain the selectivity of catalysis by the selectivity of the affinity of catalysts; it was the first to establish the existence of a correspondence between reactions and catalysts. Its main defects are that it does not explain the causes of catalysis; but only indicates the way in which it arises, and that it has nothing to say about the effect of the conditions under which the catalyst is formed.

The electron-chemical theory is concerned with the electron levels of solid catalysts and molecules, the electron-donating and electron-accepting properties of molecules, the extent to which the Brillouin zones are filled, and the equilibrium of "holes"; it divides catalytic reactions into oxidation-reduction, with electron transfer, and acid-base, with proton transfer. Each of these classes has its own catalysts. The theory is strengthened by its power to deal with promoters, for the action of which it envisages a parallelism with their action on the conductivity of semiconductors, and also with variations associated with the mode and conditions of formation of the catalyst. It is essential that this progressive theory should be developed into a more concrete form.

The multiplet theory of catalysis occupies a central position, in the sense that there are possible transitions linking it with all of the theories referred to above. The multiplet theory distinguishes reacting, index groups of atoms in the molecules, and these become applied to atoms of the catalyst lattice, being attracted to the latter by chemical forces. A consideration of actual configurations and interatomic distances leads to the discovery of the existence of structural correspondence, which enables catalysts to be selected in accordance with their structures. In this way possible catalysts for the dehydrogenation of six-membered cycles were indicated and, in particular, the catalytic activity of rhenium for the dehydrogenation of cyclohexane was predicted. A consideration of the energies of bonds within the molecules and of bonds formed with the catalyst yields energy correlations which explain selectivity.

A very complete review of the structural aspects of the multiplet theory has been given recently by Trapnell [35]. We shall enumerate the new facts that form the basis of the proof of the correctness of the multiplet sextet model for the dehydrogenation of cyclohexane hydrocarbons and the hydrogenation of benzene in presence of metals. The proof is concerned with the view that the active face (111) of a face-centered lattice, the face (100) of a hexagonal lattice, and also the ring lie flat on the surface of the catalyst.



1. Investigation of Pt, Pd, Ni, Fe, Cu and Ag alloys showed that as their compositions were changed their catalytic activity was retained so long as the structure required by the theory was retained. These results, which were obtained by Long, Frazer and Ott [36] and by Emmett and Skau [37] in 1953, were confirmed in an extensive and careful investigation by Rienäcker and Unger [38].

2. Rubinshtein, Minachev, and Shuikin [39] showed that as the Pt content of platinized charcoal was reduced the rate of hydrogenation of benzene changed symbatically with the reduction of the intensity of X-ray reflections from the face (111). Reflections from these faces disappear later than those from the others, and the catalytic activity disappears at the same time.

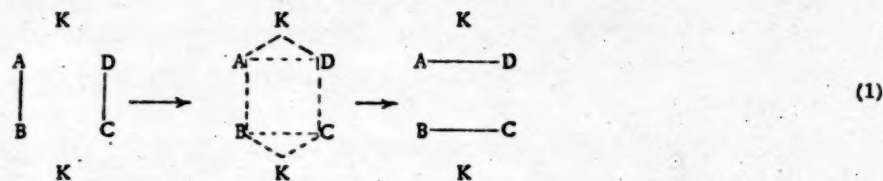
3. For a long time Beeck and others [40] considered that finely divided nickel owes its activity in hydrogenation to its (110) faces, since these faces are found on the electron-diffraction diagrams. In 1954 Sachtler, Dorgelo, and van der Knaap [41] showed by electron-microscope and electron-diffraction methods that the (110) face of the nickel lattice is oriented parallel to the substrate, but, owing to the rapid growth of (110) faces, only (111) and (100) faces remain on the surface exposed to the gas phase, so that these faces must be catalytically active in the given reactions. This is in accord with the multiplet theory.

4. According to Schuit and de Boer [42], consideration of the area occupied by hydrogen in adsorption experiments indicates that the (111) and (1000) faces of nickel are active in hydrogenation.

5. As Isagulyants has shown in our laboratory [43], cyclohexane and decahydronaphthalene are dehydrogenated with equal activation energies on platinum, and the same is true on  $\text{Cr}_2\text{O}_3$ . However, over platinum the reaction rates are different for the two compounds, whereas they are the same over  $\text{Cr}_2\text{O}_3$ . This indicates a flat disposition of the cycles on platinum and an edgewise disposition on  $\text{Cr}_2\text{O}_3$ .

6. From the measured entropy of adsorption and from the number of degrees of freedom derived from this, Kemball [44] found that benzene is adsorbed on the surface of metals such as mercury so that the plane of the ring is parallel to the metal surface.

We shall now consider doublet reactions of the type



Here the bonds A-B and C-D in the original molecules are broken and the bonds A-D and B-C are formed in the reaction products. This proceeds via the formation of an intermediate catalytic complex in which the original bonds are weakened and deformed on account of the attraction to the catalyst K; and already the formation of the bonds of the reaction products is beginning. As a limiting case of the deformation of bonds we have their complete rupture with formation of radicals attached to the surface.



Fig. 2. Model of the catalytic dehydrogenation of alcohols, top and side views. Successive stages: a)  $\text{RHCHOH} + \text{V}_2\text{W}_2 = \text{RHCHOV} + \text{HW} + \text{VW}$ ; b)  $\text{RHCHOV} + \text{VW} = \text{RHCVOV} + \text{HW}$ ; c)  $\text{RHCVOV} + 2\text{HW} = \text{RHCO} + \text{H}_2 + \text{V}_2\text{W}_2$  (V and W are catalyst valencies).

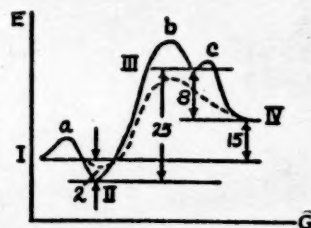


Fig. 3. Profile of potential surface for the dehydrogenation of alcohols. a, b and c denote the stages in Fig. 2. Heat changes are given in kcal/mole.

The scheme (1) implies a definite structural model, which is represented to scale for the dehydrogenation of alcohols [45] in Fig. 2. In the group  $\text{CHOH}$ , which lies on the surface, one H atom is first torn away with formation of a semihydrogenated form. The highest energy barrier is associated with the removal of the second H atom (see the broken line in Fig. 3).

The energetics of the scheme (1) and of the model in Fig. 2 are represented in Fig. 3, in which the energy level of the system is plotted to scale as ordinate, and the coordinate of the reaction is the abscissa. Denoting the energy of the bond  $\text{X-Y}$  for scheme (1) by  $Q_{XY}$ , we have:

$$\begin{aligned} E' &= -Q_{AB} - Q_{CD} + Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK} \\ E'' &= Q_{AD} + Q_{BC} - Q_{AK} - Q_{BK} - Q_{CK} - Q_{DK} \end{aligned} \quad (2)$$

In these multiplet-theory equations,  $E'$  is the energy for the formation of the multiplet complex and  $E''$  is the energy for its breakdown to form the reaction products.  $E'$  and  $E''$  correspond to the heights of the energy barriers of the reaction, and the rate of the reaction is determined by the more negative of them,  $E$ . The equations express the limiting case of the breakdown into atoms or free radicals. Actually, complete breakdown does not generally occur, but only deformation, so that for the activation energy we have

$$E \approx -\frac{3}{4}E. \quad (3)$$

Equation 2 enables us to calculate the sequence in which the different bonds react. Such calculations have been made in cases in which the bonds with the catalyst  $Q_{AK}$ , etc., are known, namely, for Ni, for which the calculated sequence was in accord with experiment in almost all of the reactions studied (several hundred) [47, 48], and also for carbon [49, 50].

Equation 2 is of interest from the point of view of the theory of the selection of catalysts [46]. Let us introduce the quantities

$$\left. \begin{aligned} u &= Q_{AB} + Q_{CD} - Q_{AD} - Q_{BC} \\ s &= Q_{AB} + Q_{CD} + Q_{AD} + Q_{BC} \\ q &= Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK} \end{aligned} \right\} \quad (4)$$

( $u$  is the heat of reaction,  $s$  is the sum of the energies of breaking and forming bonds, and  $q$  is the adsorption potential of the catalyst). Equation (2) can now be rewritten in the form

$$\left. \begin{aligned} E' &= q - s/2 + u/2 \\ E'' &= -q + s/2 + u/2 \end{aligned} \right\} \quad (5)$$

Equation 5 is represented graphically by pairs of straight lines forming "volcanolike" curves, as shown, for example, in Fig. 4, in which  $E$  is plotted as a function of  $q$ . The curves are determined only by the nature of the reaction, for the coordinates of their apexes are  $u/2$  and  $s/2$  and the slopes are  $\pm 45^\circ$ . Vertical intersecting lines correspond to  $E$ . Fig. 4 demonstrates the principles of energetic and structural correspondence that arise from the multiplet theory. Fig. 4 shows that for a given mechanism the greatest reaction rate will obtain when the vertical line passes through the apex. By determining  $E$  experimentally for a given reaction we may discover how much further the catalyst can be improved so that it may have its optimum effect ( $E_0 = u/2$ ). For this purpose it is necessary to select the energies of the bonds with the catalyst  $Q_{AK}$ ,  $Q_{BK}$ ,  $Q_{CK}$  and  $Q_{DK}$  so that their sum shall be as close as possible to the value of  $s/2$  fixed by the nature of the reaction. This is the essence of the energetic aspects of the theory of the selection of catalysts, as derived from the multiplet theory.

This part of the theory is reminiscent of the theory of color: the index group corresponds to the chromophore group, and substituents in the molecule and catalyst atoms near to the active center correspond to bathochromic and hypsochromic groups. The position of the maximum of the volcanolike curve along the axis of adsorption potentials corresponds to the position of the center of the absorption band in the spectrum. It will be clear from the above considerations that for the purposes of the theoretical selection of catalysts it is essential that experimental material should be accumulated on bond energies, particularly individual, rather than mean values.

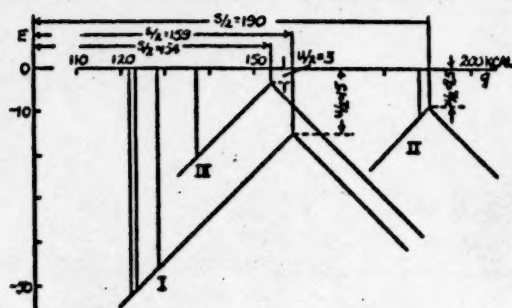


Fig. 4. Volcanolike curves: I) dehydrogenation of hydrocarbons; II) dehydrogenation of alcohols; III) dehydration of alcohols. The vertical intersects correspond to experimental values of  $E$  for  $\text{Cr}_2\text{O}_3$ .

It must be remembered that the energy of the bond with the catalyst consists, in its turn, of two components expressing 1) the energy of the bond within the crystal, and 2) the effect of surrounding atoms on it. The first quantity can be found from thermochemical tables. The sum of all the energies of the bonds of the atoms A, B, C, and D with the catalyst is the normal adsorption potential  $q_0$ .

The second quantity is associated with the position of the active center on the nonhomogeneous surface, i.e., the number and arrangement of neighboring atoms in the lattice; the presence of foreign atoms also affects it. Summing these quantities for all atoms of the active center, we obtain the quantity  $\lambda$ , the sublimation term; thus

$$q = q_0 + \lambda \quad (6)$$

This fundamental equation resolves the dispute of whether the activity of a catalyst depends on its chemical nature (G. K. Boreskov) or on the way in which it is prepared and the presence of foreign substances (as S. Z. Roginsky thought at one time). The first of these views takes only  $q_0$  into account, and the second only  $\lambda$ ; it is necessary to take both quantities into account.

It should be noted also that the method of calculation by means of Equations 2-5 is very simple mathematically and will be familiar to chemists, who calculate molecular refractions, etc., by a similar additive method. Continuing this analogy, we may state that the quantity  $\lambda$  in Equation 6 is analogous to the increments for multiple bonds. Here  $\lambda$  is a measure of the degree of unsaturation of the active centers [51, 52].

In considerations of selectivity it is necessary to examine several volcanolike curves, according to the number of possible reactions. The catalyst will be most selective for the reaction having an absolute value of  $E$  that is appreciably less than that for the other volcanolike curves.

Let us pass to the results that we obtained in 1954 in investigations along the lines that we have indicated.

We shall first consider work on the determination of the energies of bonds formed with the catalyst, which was carried out by the kinetic method. This method was proposed by the present author [46], and it consists in the experimental determination of the activation energies of several reactions selected in such a way that the number of equations for  $E$  shall be equal to the number of unknowns ( $Q_{AK}$ , etc.).

Thus, this condition is satisfied by the reactions of dehydrogenation of hydrocarbons, dehydrogenation of alcohols, and dehydration of alcohols, the index groups being:



These types of reactions, and also certain others, have been investigated in our laboratory. For the scheme (7) the first of Equations 2 is transformed into the following:

$$\left. \begin{aligned} E_1' &= -2Q_{\text{CH}} + Q_{\text{CK}} + 2Q_{\text{HK}} \\ E_2' &= -Q_{\text{CH}} - Q_{\text{OH}} + Q_{\text{CK}} + 2Q_{\text{HK}} + Q_{\text{OK}} \\ E_3' &= -Q_{\text{CH}} - Q_{\text{OH}} + 2Q_{\text{CK}} + Q_{\text{HK}} + Q_{\text{OK}} \end{aligned} \right\} \quad (8)$$

By determining  $\epsilon$  experimentally and applying Equation 3, we find  $E_1'$ ,  $E_2'$ , and  $E_3'$  and the separate energies of the bonds of the atoms C, H and O with the catalyst ( $Q_{\text{CK}}$ ,  $Q_{\text{HK}}$ , and  $Q_{\text{OK}}$ ), the values of  $Q_{\text{CH}}$  and  $Q_{\text{OH}}$  being known [47].



The results are given in Table 1.

It was found possible to construct the volcanolike curves for these reactions (Fig. 4).

It may be pointed out that the problem of the kinetics of heterogeneous-catalysis reactions is regarded as solved when the action constants and activation energies have been found, but in the present investigation the kinetics provide the solution of a problem of a higher order — the determination of bond energies.

The following substances were investigated: cyclohexane, methylcyclohexane, ethyl, isopropyl, butyl and isopentyl alcohols, 2-heptanol, cyclohexanol, formic and acetic acids, isopropyl formate, and ethyl acetate (the work was directed by A. A. Tolstopyatova and the present author and was carried out by V. A. Ferapontov, P. Teteni, I. R. Konenko and F. I. Kobos). Also, use was made of data obtained earlier by the present author and Isagulyants [43] for the dehydrogenation of cyclohexane, methylcyclohexane, dimethylcyclohexane, tetrahydronaphthalene, and

TABLE 1

Energies of Bonds with Catalyst. Results of Kinetic Determinations

Catalyst	Method of preparation	Q <sub>HK</sub>	Q <sub>CK</sub>	Q <sub>OK</sub>	Substances-
TiO <sub>2</sub>	On asbestos as ready-made oxide . . . . .	57.9	5.1	66.5	C <sub>6</sub> H <sub>12</sub> ; C <sub>2</sub> H <sub>5</sub> OH
TiO <sub>2</sub>	From TiCl <sub>4</sub> . . . . .	54.5	11.6	62.7	C <sub>6</sub> H <sub>12</sub> ; C <sub>2</sub> H <sub>5</sub> OH
ZrO <sub>2</sub>	From nitrate, precipitated with ammonia . . . . .	54.5	4.1	53.5	C <sub>6</sub> H <sub>12</sub> ; i-C <sub>3</sub> H <sub>7</sub> OH
ThO <sub>2</sub>	From nitrate, precipitated with ammonia . . . . .	66.7	5.8	62.4	CH <sub>3</sub> C <sub>6</sub> H <sub>11</sub> ; i-C <sub>3</sub> H <sub>7</sub> OH
TaO <sub>2</sub>	On asbestos . . . . .	62.7	6.0	45.0	CH <sub>3</sub> C <sub>6</sub> H <sub>11</sub> ; i-C <sub>3</sub> H <sub>7</sub> OH
Cr <sub>2</sub> O <sub>3</sub>	Precipitated with sodium carbonate . . . . .	56.3	6.0	69.5	CH <sub>3</sub> C <sub>6</sub> H <sub>11</sub> ; i-C <sub>3</sub> H <sub>7</sub> OH
Cr <sub>2</sub> O <sub>3</sub>	Precipitated with ammonia . . . . .	58.1	14.1	51.7	CH <sub>3</sub> C <sub>6</sub> H <sub>11</sub> ; i-C <sub>3</sub> H <sub>7</sub> OH
Cr <sub>2</sub> O <sub>3</sub>	On asbestos, precipitated with sodium carbonate . . . . .	62.1	6.8	43.0	CH <sub>3</sub> C <sub>6</sub> H <sub>11</sub> ; i-C <sub>3</sub> H <sub>7</sub> OH
Cr <sub>2</sub> O <sub>3</sub>	On asbestos, from ammonium dichromate . . . . .	59.1	9.8	33.1	CH <sub>3</sub> C <sub>6</sub> H <sub>11</sub> ; i-C <sub>3</sub> H <sub>7</sub> OH
		58.2	4.7	49.7	C <sub>6</sub> H <sub>12</sub> ; i-C <sub>3</sub> H <sub>7</sub> OH; HCOOH
MoO <sub>3</sub> O <sub>5</sub>	On asbestos . . . . .	44.7	18.2	63.5	C <sub>6</sub> H <sub>12</sub> ; i-C <sub>3</sub> H <sub>7</sub> OH; HCOOH
W <sub>2</sub> O <sub>5</sub>	On asbestos . . . . .	48.5	16.3	53.3	CH <sub>3</sub> C <sub>6</sub> H <sub>11</sub> ; i-C <sub>3</sub> H <sub>7</sub> OH
WS <sub>2</sub>		60.5	16.4	51.3	CH <sub>3</sub> C <sub>6</sub> H <sub>11</sub> ; i-C <sub>3</sub> H <sub>7</sub> OH
Ni		53	7	59	Thermochemical determination
ThO <sub>2</sub>	From nitrate, precipitated with ammonia . . . . .	Q <sub>HK</sub> 53.3	Q <sub>CK</sub> 18.6	Q <sub>NK</sub> 21.0	1,2,2-Trimethylpropylamine
Th <sub>2</sub> O	From nitrate, precipitated with ammonia . . . . .	53.9	19.3	37.7	α-Ethylbenzylamine

tetrahydro-2-methylnaphthalene, these data being supplemented by A. A. Tolstopyatova, who investigated the catalysis of alcohols over the same catalyst. Further, in conjunction with N. A. Vasyunina, an investigation was made into the catalysis of amines, namely, 1-methylhexylamine, diisopropylamine, 1,3-dimethylbutylamine, 1,2,2-trimethylpropylamine, α-ethylbenzylamine, N<sup>1</sup>,N<sup>1</sup>-diethyl-1,4-pentanediamine. From these data together with the data on the catalysis of hydrocarbons by the authors already mentioned and by A. A. Tolstopyatova we succeeded in calculating the energy of the bond formed by nitrogen with the catalyst.

As catalysts we took oxides of metals of the even groups of Mendeleev's system [54]:

From Group II: Be, Mg, Ca, Sr, Ba, Zn, Cd.

From Group IV: Ti, Zr, Th.

From Group VI: Cr, Mo, W.

Preparations of WS<sub>2</sub> and of Ni on Al<sub>2</sub>O<sub>3</sub> were also investigated. The percentage conversions were determined experimentally under identical conditions, the extent to which reaction occurred being small. From these results, Arrhenius straight lines were constructed which gave a good fit to the experimental points. Diffusion did not play any part, the truth of this statement being verified in selected cases, in which it was shown that the grain size of the catalyst had no effect on the reaction rate.



The oxides of elements of Group II were found to be unsuitable for such investigations, since, although they effected the dehydrogenation and dehydration of alcohols (in the present investigation  $\epsilon$  was measured in these cases), they did not effect the dehydrogenation of hydrocarbons, in spite of indications to the contrary in the literature [55].

It was found possible to make use of the results on the reactions over oxides of Group IV and Group VI metals (it should be noted that some of these reactions were effected for the first time over these particular catalysts). The following results were obtained.

1. The activation energies for identical index groups having different substituents were found to be identical. By way of example we may quote data for the dehydrogenation over  $\text{Cr}_2\text{O}_3$  of cyclohexane ( $\epsilon = 28.5$ ), methylcyclohexane ( $\epsilon = 26.6$ ), and 1,3-dimethylcyclohexane ( $\epsilon = 24.8$ ), and also for the dehydrogenation over Ni on  $\text{Al}_2\text{O}_3$  of 1-methylhexylamine ( $\epsilon = 9.4$ ), 3-methyl-1-propylbutylamine ( $\epsilon = 9.6$ ), diisopropylamine ( $\epsilon = 8.6$ ), and  $\text{N}^1, \text{N}^1$ -diethyl-1,4-pentanediamine ( $\epsilon = 10.7$  kcal/mole). This indicates, in agreement with theory, that the molecules are oriented identically on the catalyst.

2. Calculation yields values of  $Q_{EK}$  (by  $Q_{EK}$ , here and below, we understand the quantities  $Q_{AK}$ , etc.) of the expected order of magnitude.

3. For a given index the substituents have usually little effect on  $Q_{EK}$ . There is a scatter in the values for different catalysts, and also for different methods of preparing the catalysts, which is a reflection of the effect of  $\lambda$ . As indicated by Equation 6, this is in accord with theory.

4. The value found from the kinetics for  $Q_{HK}$  and  $Q_{CK}$  are often close to the thermochemical values, for example [56]  $Q_{HCr} = 56.3$  (kinetic),  $Q_{HNI} = 53$  (thermochemical);  $Q_{CCr} = 6.0$  (kinetic),  $Q_{CCr} = 7$  (thermochemical). The value of  $Q_{HK}$  varies only little in the reactions investigated. In one case a very much lower value,  $Q_{HK} = 44.7$ , was observed, from which it follows that the constancy is real and is not a mathematical artifact.  $Q_{CK}$  is a small quantity, and owing to its smallness the mode of formation of the catalyst has a great effect on its value; it sometimes suffers a twofold variation.

The fact that the oxides of elements of Group II do not promote the dehydrogenation of hydrocarbons, but bring about the catalysis of alcohols is probably to be explained as follows. Here  $Q_{HK}$  and  $Q_{CK}$  are small and are unable to bring about the lowering of  $E$  that is necessary for the dehydrogenation of hydrocarbons.  $Q_{OK}$ , on the contrary, is great, which is a deciding factor for the possibility of the dehydrogenation and dehydration of alcohols. This view is confirmed by the well-known fact that Group II metals have a high affinity for oxygen.

5. The bond  $\text{O}-\text{K}$  is found to be much more sensitive to various influences, so that  $Q_{OK}$  is much less constant. As will be seen from Table 1,  $Q_{OH}$  depends a) on neighboring atoms (the method of preparation) and substituents, and b) on the position of the element in Mendeleev's system.

6. The sequence of changes in  $Q_{OH}$  in a column of Mendeleev's stable does not correspond to the sequence of  $Q_{OK}$ , determined kinetically (see Table 1) and thermochemically, for we have:

$$\text{Ti}-\text{O} \dots 84.0; \text{Zr}-\text{O} \dots 94.0; \text{Hf}-\text{O} \dots 97.4; \text{Th}-\text{O} \dots 102.8.$$

It is probable that this noncorrespondence is to be explained by screening with other O atoms. In the approach of an oxygen atom from a molecule to a metal atom of small radius there is repulsion effect due to neighboring oxygen atoms in the lattice. This explanation is confirmed by thermochemical data, which show that as oxygen atoms accumulate in an oxide the mean bond energy falls; thus, the mean  $Q_{OCr}$  for  $\text{Cr}_2\text{O}_3$  is 79, whereas for  $\text{CrO}$ , it is 53.

7. For the dehydrogenation and deamination of amines over  $\text{ThO}_2$  (see Table 1)  $Q_{HK}$  and  $Q_{CK}$  were found to be close to the corresponding quantities for alcohols. The energy for the bond with the catalyst  $Q_{NK}$  was found to fall regularly between the values for C and O:

$$Q_{CK} < Q_{NK} < Q_{OK}.$$

The energy of the bond  $\text{N}-\text{K}$  is greatly affected by substitution in the molecule: when the substituent is aromatic  $Q_{NK} = 37.7$ , and when it is aliphatic  $Q_{NK} = 21.0$ . In its sensitivity to such effects the bond  $\text{N}-\text{K}$  is analogous to the bond  $\text{O}-\text{K}$ .

In such a new field as that which we are now considering there are naturally many problems that have not yet been investigated. As a result it was necessary to make several simplifying assumptions in the preceding calculations, and we shall now pass to a consideration of these assumptions.

1. The mechanism of both dehydrogenation and dehydration is assumed to be atomic, and not ionic. For dehydrogenation no doubts can arise, and we consider that convincing evidence for the atomic mechanism of dehydration is provided by a comparison of the regularities revealed by the work of Neiman and Shapavalov [57] on the one hand and of Bork [58] on the other (see Table 2). Experiments on the exchange of alkyl halides with bromine and iodine showed that with increase in the extent of substitution the rate constant  $k$  falls and the activation energy rises in ionic reactions, whereas the reverse is true in atomic reactions. In the dehydration of alcohols over  $Al_2O_3$  the constants change with increase in the extent of substitution in the direction required by the atomic mechanism, thus confirming that the reaction occurs by this mechanism. By this we do not wish to imply that the ionic mechanism does not occur in presence of acidic catalysts, such as phosphoric acid on charcoal, or of aluminosilicates; on the contrary, the ionic mechanism does occur in these cases (cf. [59]). In this we are at variance with opinions, e.g. those of Dowden [60], which assert that dehydration is always an ionic reaction.

TABLE 2

Comparison of Atomic and Ionic Reaction Mechanisms

Reacting substance	Atom exchange (% per hour)	Ion exchange		Literature reference
		k	$\epsilon$	
$CH_3I$	0.03	1,200	15,400	[57]
$CH_3(CH_2)_4I$	0.05	65	19,000	[57]
$CH(CH_3)_2I$	1.4	10	20,500	[57]
	$k_{app}$	$\epsilon$		
$CH_3CH_2OH$	28.4	20,210		[58]
$CH_3CH_2CH_2OH$	55.4	18,330		[58]
$(CH_3)_2CHCH_2OH$	52.7	16,450		[58]

2. The dehydration of alcohols proceeds, as Topchieva and coworkers have shown [19], via a surface alkoxide. We assume that the role of the alkoxide in dehydration is analogous to that of the semihydrogenated form in dehydrogenation. As shown above, the existence of a semihydrogenated form finds its place in the scheme of calculation adopted, and the same is true of the alkoxide.

3. The reactions under comparison should be carried out at the same active centers. However, if the differences in the latter are not great, then they have little effect in the results in view of the form of the equations for determining  $Q_{EK}$ .

4. The rate of reaction should rise with decrease in  $\epsilon$ . The experimental results show that we are indeed dealing here with a classical case of this kind.

5. All reactions are first-stage reactions, i.e. are held back by the stage of forming the intermediate complex. This is confirmed by the fact that in Figures 4 and 5 the intersecting lines are to the left of the maxima of the volcanolike curves.

6. The mean, and not individual, values of the bond energies are taken. This is justified by the fact that compensation of the effect of neighboring atoms on  $Q_{AB}$  etc. and on  $Q_{AK}$  etc. occurs to an appreciable extent [34]. When there are great variations there is no such approximate compensation, and this has been noted above, for example, for the effect of the aromatic nucleus.

7. The activation energies used in the calculation are true values, not apparent. This is confirmed by the fact that the process occurs in the kinetic region (see above) and that in the simplest cases the relative adsorption coefficients are not great, and calculation shows that in these cases the percentage conversion can be taken instead of rate constants. For more precise results it is essential to use the full formula.

8. It is assumed that proportionality coefficient in Equation 6 is  $3/4$ . It should be noted that the value of  $Q_{EK}$  is not very sensitive to small changes in this coefficient; thus, a calculation in which the coefficient is given the value of unity gives an only slightly different value of  $Q_{EK}$ . It should be noted also that Semenov [4], using an independent method, again arrives at a coefficient of  $3/4$  for a similar case.

The following question now arises. When the energies of the bonds formed with the catalyst have been determined, in what way can they be utilized? It is clear that when many such values are known for substances of various chemical nature and when the laws relating them to the method of preparation are known it will be possible to make use of values of  $Q_{EK}$  in the selection of catalysts by the method indicated above, but even now the existing data permit us to solve the problem that is symmetrical with respect to the problems of choice of catalysts.

In the selection of catalysts the reaction is fixed and catalysts are sought for it. In the symmetrical problem we may fix the catalyst and determine what reactions can proceed on it and to what extent.

In this connection the present author and Ponomarev [61] have examined the reactions of furan derivatives over a catalyst of a given chemical nature — nickel — for which the value of  $Q_{EK}$  is known. In this case also, the method of volcanolike curves based on the multiplet theory is applicable. It must be particularly emphasized that in the exposition that follows none of the above-mentioned simplifying assumptions are made. The coordinates of the apexes of the volcanolike curves for the reactions occurring are given in Table 3. Values of  $E'$  are also given in the table. The calculation was made with the aid of Equation 5 and was based on values of  $Q$  from a previous paper [47] and on a value for the energy of the stabilization of the furan ring of  $\sigma = 16$  kcal [62].

Table 3

Theoretical Sequence of Reactions over a Nickel Catalyst

No.	Reaction	Doublet scheme	$u$ (kcal)	$s$ (kcal)	$E'$ (kcal)
1	Hydrogenation of the olefin bond	$\begin{array}{c} \text{C} \text{ H} \\ \text{C} \text{ H} \end{array}$	30	318	6
2	Hydrogenation of the carbonyl bond	$\begin{array}{c} \text{C} \text{ H} \\ \text{O} \text{ H} \end{array}$	15	379	5
3	Hydrogenation of the first double bond in the furan ring	$\begin{array}{c} \text{C} \text{ H} \\ \text{C} \text{ H} \end{array}$	11.4	334	< 5.7; 3
4	Formation of a spiro compound from furfuryl alcohol	$\begin{array}{c} \text{C} \text{ O} \\ \text{C} \text{ H} \end{array}$	6	308	< 5; 2
5	Hydrogenolysis of the carbon-oxygen bond	$\begin{array}{c} \text{C} \text{ H} \\ \text{O} \text{ H} \end{array}$	24	370	-1
6	Hydrogenolysis of the carbon-carbon bond	$\begin{array}{c} \text{C} \text{ H} \\ \text{C} \text{ H} \end{array}$	12	336	-42

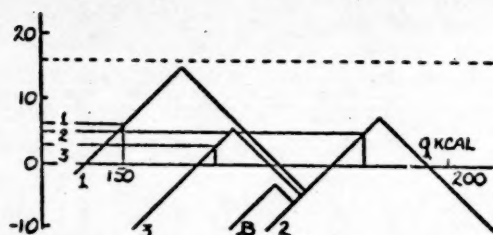


Fig. 5. Volcanolike curves for the hydrogenation of furan and benzene derivatives. (For numbering of the reactions see Table 3.  $E$  and  $q$  are in kcal).

displaced upward by about 16 kcal [46] (broken line in Fig. 5). Hence, all the values of  $E'$  in Table 3 are actually negative. In the cyclization of a furan compound to form a spiran, one (external) double bond in the furan ring is first hydrogenated [63]: in reaction No. 4 (for the numbering of the reactions see Table 3) occurring at the surface, the valency angle is deformed, so that the value of  $E'$  is lowered somewhat. Corrected values of  $E'$  for reactions No. 3 and 4 are also given in Table 3.

Thus, the multiplet theory leads us to the following rule: in the hydrogenation of furan derivatives the reactions occur in a definite sequence according to the difficulty with which they proceed, i.e., in order of diminishing  $E'$  (Table 3). For example, in accordance with the rule, in the hydrogenation of 1-(2-furyl)-1-penten-3-one

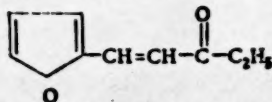




TABLE 4

Sequence of Reactions in the Hydrogenation of Furan Compounds over Nickel (Comparison of experimental and theoretical data) Abbreviations: F = 2-furyl; TH = tetrahydro; dioxaspiran = 1,6-dioxaspiro[4.4]nonane; NIR = Raney nickel; NiK = Ni on kieselguhr

Original substance	Substance formed	A	Catalyst	Temp. (°C)	Pressure (atm)
1	2	3	4	5	6
Transformations attaining stage 1,2. Average temperature 30°					
2-Furanacrolein	2-Furanpropionaldehyde	1,236	NiR	23	100
4 F-3-buten-2-one	4-F-2-butanone	1,236	NiR	20	50
1-F-8-methyl-1-octen-3-one	1-F-3-octanone	1,236	NiR	20	1
1,3 DiF 2 propen-1-one	1,3-DiF-1-propanone	1,236	NiR	50	100
1,5-DiF-1,4-pentadien-3-one	1,5-DiF-3-pentanone	1,236	NiR	20	1
Transformations attaining stage 1,3. Average temperature 40°					
Vinylfuran	Ethylfuran	1,36	NiK	65	250
		1,36	NiR	15	75
Transformations attaining stage 2,3. Average temperature 85°					
2-Furaldehyde	Furfuryl alcohol	2,356	Ni	160	65
2-Furanacrolein	2-Furanpropanol	12,356	NiR	80	—
6 F-3,5-hexadien-2-one	α-Methyl-2-furanpentanol	12,356	NiR	20	1
Transformations attaining stage 3,2°					
1-F-5-methyl-1-hexen-3-one	5-Methyl-1-THF-3-hexanone*	13,256	Ni	—	—
Furfurylidene camphor	THfurfurylcamphor*	13,256	Ni	—	—
Transformations attaining stage 3,4. Average temperature 130°					
2 Furanpropanol	TH-2-furanpropanol	13,456	NiK	100	150
5-Methyl-2-furanpropanol	TH-5-methyl-2-furanpropanol	13,456	NiK	120	150
α-Methyl-2-furanpropanol	TH-α-methyl-2-furanpropanol	13,456	NiK	100	150
α,5-Dimethyl-2-furanpropanol	TH-α,5-dimethyl-2-furanpropanol	13,456	NiK	120	128
α-Ethyl-2-furanpropanol	α-EthylTH-2-furanpropanol	13,456	NiK	120	96
α-Propyl-2-furanpropanol	TH-α-propyl-2-furanpropanol	13,456	NiK	120	120
α-Butyl-2-furanpropanol	α-ButylTH-2-furanpropanol	13,456	NiK	120	99
α-Pentyl-2-furanpropanol	TH-α-pentyl-2-furanpropanol	13,456	NiK	120	150
α-Isohexyl-2-furanpropanol	α-IsohexylTH-2-furanpropanol	13,456	NiK	120	103
α-Phenyl-2-furanpropanol	TH-α-phenyl-2-furanpropanol	13,456	NiK	125	142
α-Phenethyl-2-furanpropanol	TH-α-phenethyl-2-furanpropanol	13,456	NiK	120	142
β-Methyl-α-phenyl-2-furanpropanol	TH-β-methyl-α-phenyl-2-furanpropanol	13,456	NiK	140	110
2-Furanpropionaldehyde	TH-2-furanpropanol	123,456	NiK	160	150
1,5-DiF-3-pentanol	1,5-BisTHF-3-pentanol	13,456	NiR	120	100
1-F-3-phenyl-1,3-propanedione	1-THF-3-phenyl-1,3-propanediol	123,456	NiR	125	170
1 F-1,3-butanedione	1-THF-1,3-butanediol				
2-Furanacrolein	TH-2-furanpropanol	123,456	NiR	160	150
α-Ethyl-2-furanacrolein	β-Ethyl-TH-2-furanpropanol	123,456	NiR	175	150
4 F-3-buten-2-one	TH-α-methyl-2-furanpropanol	123,456	Ni	125	100
1,3-DiF-2-propen-1-one	α-THFTH-2-furanpropanol	123,456	NiR	130	115
Difurfurylidene cyclohexanone	BisTHfurfurylcyclohexanol	123,456	NiR	175	150
1 F-1-hexen-3-one	TH-α-propyl-2-furanpropanol	123,456	NiR	200	70
Transformations attaining stage 3,5. Average temperature 130°					
Furan	THfuran	13,56	NiR	170	—
	Butyl alcohol				
2 Methylfuran	TH-2-methylfuran	13,656	Ni	200	—



TABLE 4 (continued)

1	2	3	4	5	6
2-Ethylfuran	2-EthylTHfuran	13,56	NiR	<110	70
2-Propylfuran	TH-2-propylfuran	13,56	NiR	<110	70
2-Pentylfuran	TH-2-pentylfuran	13,56	NiR	110	70
2-(1-Butenyl)furan	2-ButylTHfuran	13,56	NiR	100	50
2-Benzylfuran	2-BenzylTHfuran	13,56	Ni	100	50
2,5-Dimethylfuran	TH-2,5-dimethylfuran	13,56	NiR	200	70
Furfuryl alcohol	THfurfuryl alcohol	13,56	NiR	80	80
$\alpha$ -Methylfurfuryl alcohol	TH- $\alpha$ -methylfurfuryl alcohol	13,56	NiR	75	10
$\alpha$ -Ethylfurfuryl alcohol	$\alpha$ -EthylTHfurfuryl alcohol	13,56	NiR	65	80
$\alpha$ -Propylfurfuryl alcohol	TH- $\alpha$ -propylfurfuryl alcohol	13,56	NiR	65	80
$\alpha$ -Phenylfurfuryl alcohol	TH- $\alpha$ -phenylfurfuryl alcohol	13,56	NiK	65	80
$\alpha$ -Methyl-2-furanpentanol	TH- $\alpha$ -methyl-2-furanpentanol	13,56	NiK	120	90
2-Furaldehyde diethyl acetal	TH-2-furaldehyde diethyl acetal	13,56	NiR	175	—
2-Furaldehyde ethylene acetal	TH-2-furaldehyde ethylene acetal	13,56	NiK	125	150
Furoin	1,2-BisTHF-1,2-ethanediol	123,56	NiR	150	150
5-(Hydroxymethyl)-2-furaldehyde	TH-2,5-furandimethanol	123,56	NiK	160	70
2-Furaldehyde	THfurfuryl alcohol	123,56	NiK	125	40
5-F-2,4-pentadienal	TH-2-furanpentanol	123,56	NiR	175	150
6-F-3,5-hexadien-2-one	TH- $\alpha$ -methyl-2-furanpentanol	123,56	NiR	175	150
7-F-4,6-heptadien-3-one	$\alpha$ -EthylTH-2-furanpentanol	123,56	NiR	140	100
1,9-DiF-1,3,6,8-nonateuraen-5-one	1,9-BisTHF-5-nonanol	123,56	NiR	175	180
Transformations attaining stage 4,5. Average temperature 130°					
2-Furanpropanol	Dioxaspiran	134,56	NiK	100	150
$\alpha$ -Methyl-2-furanpropanol	2-Methyldioxaspiran	134,56	NiK	100	150
5-Methyl-2-furanpropanol	2-Methyldioxaspiran	134,56	NiK	120	150
$\alpha$ ,5-Dimethyl-2-furanpropanol	2,7-Dimethyldioxaspiran	134,56	NiK	120	140
$\alpha$ -Ethyl-2-furanpropanol	2-Ethyldioxaspiran	134,56	NiK	120	96
$\alpha$ -Propyl-2-furanpropanol	2-Propyldioxaspiran	134,56	NiK	120	128
$\alpha$ -Butyl-2-furanpropanol	2-Butyldioxaspiran	134,56	NiK	120	99
$\alpha$ -Pentyl-2-furanpropanol	2-Pentyldioxaspiran	134,56	NiK	120	150
$\alpha$ -Isohexyl-2-furanpropanol	2-Isohexyldioxaspiran	134,56	NiK	120	103
$\alpha$ -Phenyl-2-furanpropanol	2-Phenyldioxaspiran	134,56	NiK	125	142
$\beta$ -Methyl- $\alpha$ -phenyl-2-furanpropanol	3-Methyl-2-phenyldioxaspiran	134,56	NiK	140	110
1,5-DiF-3-pentanol	2-(2-THFethyl)dioxaspiran	134,56	NiR	120	105
2-Furanpropionaldehyde	Dioxaspiran	1234,56	NiK	160	150
2-Furanacrolein	Dioxaspiran	1234,56	NiR	175	150
$\alpha$ -Ethyl-2-furanacrolein	3-Ethyldioxaspiran	1234,56	NiR	175	150
4-F-3-buten-2-one	2-Methyldioxaspiran	1234,56	NiR	175	150
Transformations attaining stage 5,5. Average temperature 190°					
THfuran	Butyl alcohol	5,56	NiR	90	155
2-Methylfuran	2-Pentanol	135,56	NiR	200	—
3-F-acrylophenone	2-(3-Phenylpropyl)THfuran	1235,56	NiR	140	135
TH-2-methylfuran	2-Pentanol	5,56	Ni	230	140
Dioxaspiran	TH-2-furanpropanol	5,56	NiK	200	150
Transformations attaining stage 5,6. Temperature > 310°					
2-Furanacrolein	Heptane	12345,6	NiO+ +MoS <sub>3</sub>	310	100
2-Furanacrolein	Heptane	12345,6	Ni	>300	100
$\alpha$ -Methylfurfuryl alcohol	Heptane	12345,6	NiO+ +MoS <sub>3</sub>	340	100
Furan	Butane	135,6	Ni	>300	—
THfuran	Butane	35,6	Ni	>300	—

over nickel the following should be formed successively: 1) 1-(2-furyl)-3-pentanone; 2)  $\alpha$ -ethyl-2-furanpropanol; 3)  $\alpha$ -ethyltetrahydro-2-furanpropanol; 4) 2-ethyl-1,6-dioxaspiro[4.4]nonane



5) nonane; and 6) methane.

Verification of this rule on the basis of experimental material is carried out in Table 4. The numbers in the column headed A, for example 123,456 indicate that in the given change reactions No. 1, 2, and 3 (Table 3) have already occurred, but the reactions No. 4, 5, and 6 have not yet occurred, the change having attained the stage 3,4. Here, each of the reactions No. 1, 2, and 3 proceeds more readily than each of the reactions No. 4, 5, and 6. Underlined digits in Table 4 indicate secondary reactions that are possible owing to the completion of primary reactions:  $1 \rightarrow 6$ ,  $2 \rightarrow 5$ ;  $3 \rightarrow 1,4$  and  $6$ ;  $4 \rightarrow 5$  and  $6$ . In A numbers on one side of the comma are not repeated. Reactions that depend on reactions that have not yet occurred are not shown in A. When the digits in column A of Table 4 are in ascending order (or do not diminish), it means that the theoretical rule that we have found is correct. Table 4 gives the known examples [61] of the changes undergone by furan compounds when hydrogenated over Ni (apart from those of a few containing the groups  $-(CO)-O-$  and  $-N-$ ).

Table 4 shows that theory is in excellent agreement with experiment for more than 80 transformations. Exceptions are rare; they are indicated in the table by asterisks.

It will be seen from Table 4 that in all cases in which a molecule contains both a furan and a benzene ring, the former is more readily hydrogenated, in accord with the requirements of theory.

It can also be seen from Table 4 that, in accord with theoretical predictions, the temperature required for the reaction is generally higher, the higher the number of the reaction in Table 3. This is all the more remarkable in that the hydrogenation reactions of furan compounds have been carried out independently by various workers, who had only preparative aims in view. In accordance with theory, different sequences are found over other catalysts [66, 67].

The discovery of the laws regulating the hydrogenation of furan derivatives is of great practical importance, since these processes are associated with a new important trend in the industrial utilization of agricultural wastes.

In conclusion I should like to appeal to those present to join forces in working for the solution of the particularly important problem of the scientific selection of catalysts. The object of this paper was to show what foundations exist for this work. It must be remembered that in the discussions experiment must be the judge and that the general goal of our endeavors is the welfare of our Fatherland.

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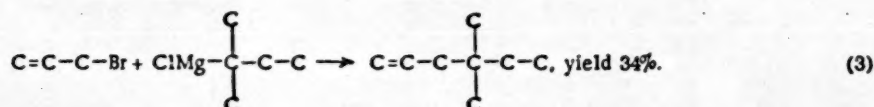
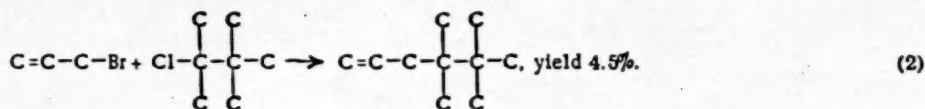
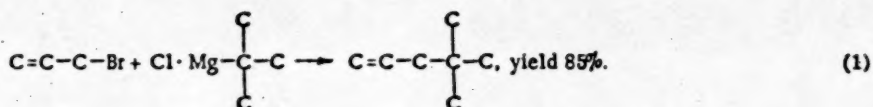
# SYNTHESIS OF BRANCHED ALIPHATIC HYDROCARBONS VIA 2-ALKENYL HALIDES

A. D. Petrov

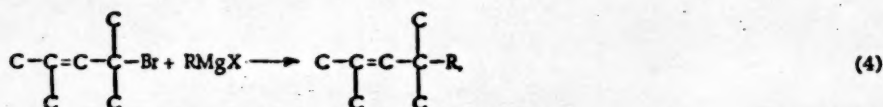
(Paper read at a general meeting of the Division of Chemical Sciences  
of the Academy of Sciences of the USSR, March 21, 1955)

2-Alkenyl halides have received extensive application during the last 10-15 years for the synthesis of branched alcohols and hydrocarbons, mainly in connection with the intensive exploitation of organomagnesium synthesis with the object of preparing model individual hydrocarbons present in fuels and oils.

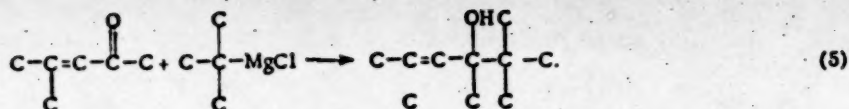
It has been established that 2,2-dimethylpentane is best prepared via 4,4-dimethyl-1-pentene, which can be synthesized in 85% yield, calculated on the amount of allyl bromide taken, by addition to the latter of an ethereal solution of tert-butylmagnesium chloride [1], whereas in the condensation of tert-butyl chloride with propylmagnesium bromide, even under special conditions (heating to 80°, or in presence of HgCl<sub>2</sub>), the yield of 2,2-dimethylpentane does not exceed 20% [2]. As Liberman and Kazansky [3] showed, the yield of 4,4-dimethyl-1-hexene obtained when 1,1-dimethylpropylmagnesium halide is added to allyl bromide is 34%, but in the condensation of 2-chloro-2,3,3-trimethylbutane with allyl bromide under Yarovsky's conditions the yield of 4,4,5,5-tetramethyl-1-hexene does not exceed 4.5% [4]:



The high reactivity of 2-alkenyl halides found wide application in the work of Levina and coworkers [5], who condensed 4-bromo-2,4-dimethyl-2-pentene, which on account of its structure is unable to undergo the allyl rearrangement, with various alkylmagnesium halides. The reaction gave yields of 25-30%:



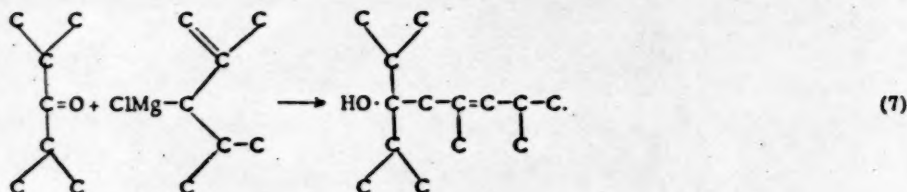
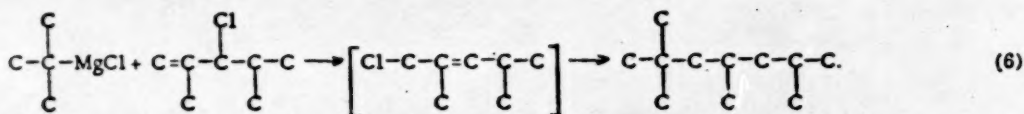
Petrov, Koptev and Kaplan [6] showed that steric difficulties in the condensation of a branched ketone with branched alkyl halides could be overcome by introducing a double bond into the ketone, instead of into the alkyl halide, but again in the  $\beta$ -position with respect to the functional group, the oxygen of the carbonyl. Thus, tert-butylmagnesium chloride, which does not give a tertiary alcohol with 4-methyl-2-pentanone, but only reduces it, reacts with mesityl oxide at 0° with formation of a tertiary alcohol and the diolefin resulting from its dehydration:



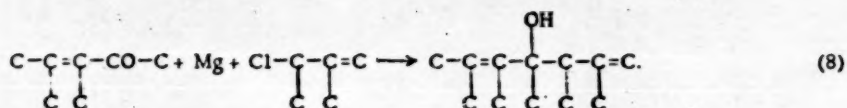
The possibility of increasing the yield by introduction of a double bond in either reaction component greatly widens the prospect for the synthesis of branched compounds.

Since there are comparatively few alkenyl halides of the allyl type that are unable to undergo the allyl rearrangement on account of their structure, we frequently meet the problem of suppressing such isomerization either by the selection of a second component of suitable structure or by selection of the condensation conditions.

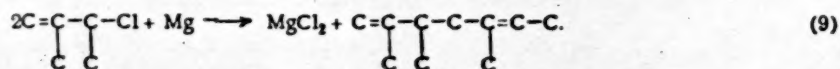
Petrov and Ponomarenko [7] showed that in the course of the organomagnesium synthesis 3-chloro-2,4-dimethyl-1-pentene isomerizes completely into the corresponding primary chloride in reactions both with tertiary and with primary alkylmagnesium halides and also in the reaction of condensation with 2,4-dimethyl-3-pentanone in presence of magnesium:



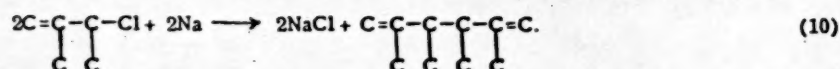
However, as has been shown in the present series of investigations by Petrov and Melekhin, the analogous allyl halide 3-chloro-2-methyl-1-butene reacts with unsaturated branched ketones, such as mesityl oxide and 3-methyl-3-buten-2-one, without isomerization, probably owing to the high rate of the condensation reaction:



Petrov, Melekhin and Sushchinsky [8] have shown that in the condensation of two molecules of 3-chloro-2-methyl-1-butene in presence of magnesium one molecule of the chloro compound undergoes allyl rearrangement and 2,3,5-trimethyl-1,5-heptadiene is formed:

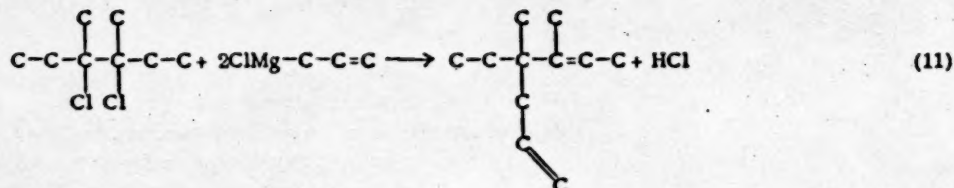


When the same alkenyl halide is condensed in presence of sodium, the isomerization becomes a subordinate reaction and the main product is 2,3,4,5-tetramethyl-1,5-hexadiene:



In the condensation of 3-chloro-2-methyl-1-butene in presence of potassium, which is even more alkaline in character than sodium and brings about a more rapid reaction even at lower temperatures, isomerization occurs to an extremely small extent. Hence, the occurrence of the allyl rearrangement can be avoided not only by selecting carbonyl and halogen compounds of suitable structure, but also by selecting suitable conditions of condensation, and this possibility promises to extend greatly the scope of this method of synthesizing branched hydrocarbons. We

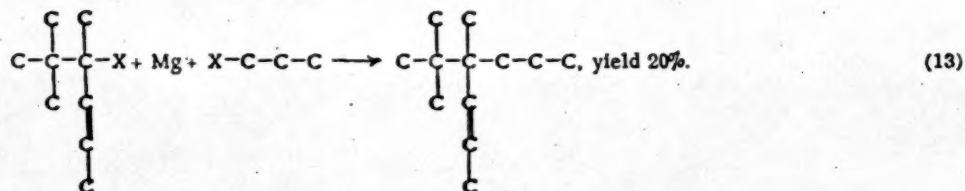
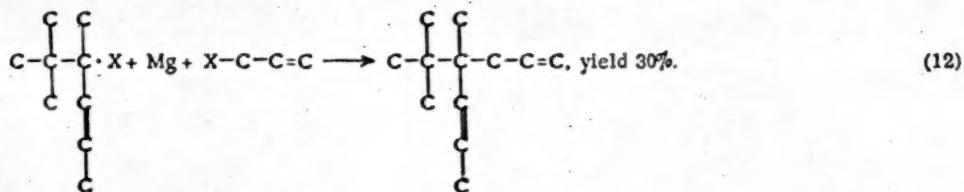
will give one further example of the effect of the condensation conditions on the character of the products. It was shown recently by Petrov and Shebanova [9] that in the treatment of 3,4-dichloro-3,4-dimethylhexane with allylmagnesium chloride at room temperature condensation occurred with only one molecule of allyl halide with simultaneous elimination of a molecule of HCl:



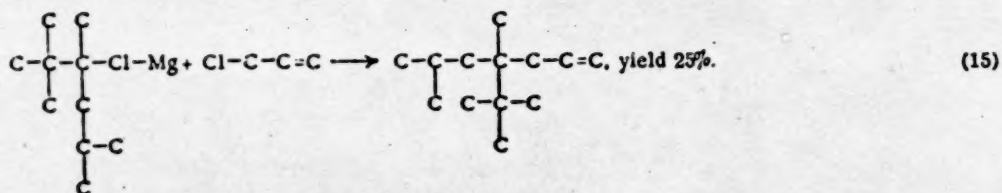
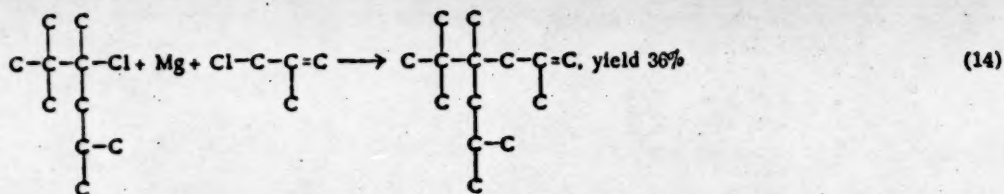
By carrying out the condensation at  $-10^\circ$ , we have succeeded in the present investigation in obtaining not only this  $\text{C}_{11}$  hydrocarbon (in about 15% yield), but also the desired  $\text{C}_{14}$  diene, which was hydrogenated with formation of 4,5-diethyl-4,5-dimethyloctane.

It was pointed out above that in condensations with ketones having  $\alpha,\beta$ -double bonds (i.e., characterized by  $\pi,\pi$ -conjugation) even allyl halides that can undergo the allyl rearrangement do not, in fact, isomerize, evidently owing to the particularly high rates of reaction that obtain in this case, i.e., the case in which a conjugated system is found in both reaction components.

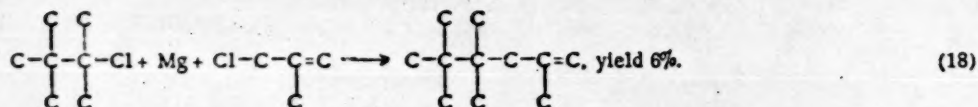
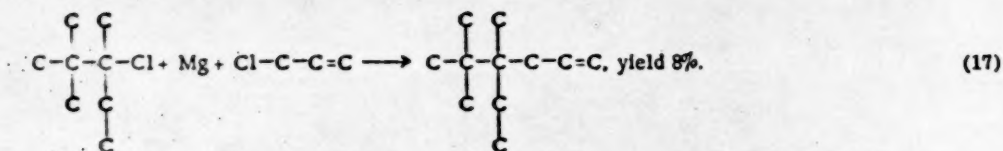
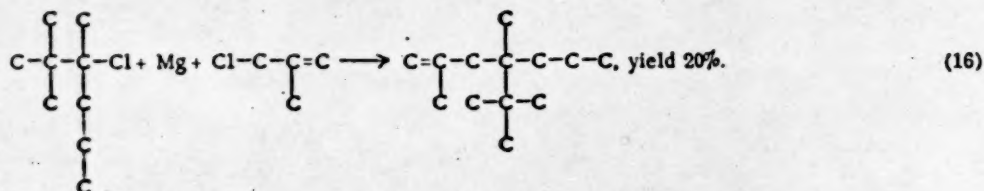
Recently, while working on the problem of finding 2-alkenyl halides that do not undergo the allyl rearrangement (on account of various steric or electronic effects) in condensations not only with alkenyl halides but also with alkyl halides, Petrov and Lavrishcheva [10] made the following observation. It was found that the tertiary alcohol synthesized from pinacolone and  $\text{BrMgC}=\text{C}=\text{C}$  forms an active halogen derivative having a double bond in the  $\beta$ -position, and that this reacts with  $\text{RMgX}$  (R may be allyl or propyl) without undergoing the allyl rearrangement. This peculiarity of the halogen compound is not shared by such compounds as 4-bromo (or chloro)-4-methyl-1-pentene (in the formation of which the double bond is not displaced from the allyl to the propenyl position, so that these halogen compounds are inactive), nor by other tertiary halogen compounds containing allyl radicals and undergoing the allyl rearrangement in the course of their formation, and this halogen compound (4-chloro-4,5,5-trimethyl-2-hexene) may be used in the synthesis of hydrocarbons containing two adjacent quaternary carbons:



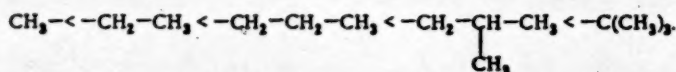
The high yields attained (in comparison with those obtained in the condensation of an allyl halide with 2-chloro-2,3,3-trimethylbutane (Equation 2) were at first attributed by us solely to the occurrence of  $\sigma,\pi$ -conjugation in both components in the first case, but in one component only in the second. Continuing this investigation, Petrov and Sushchinsky replaced allyl by 2-methylallyl in the tertiary halide, but this made it necessary to hydrogenate the unsaturated tertiary alcohol before its conversion into the halogen compound. The reactions of Equations 14 and 15 were carried out, and it was found that saturated but asymmetrical tertiary chloro compounds analogous to 2-chloro-2,3,3-trimethylbutane give condensation products in yields that differ little from those obtained from 2-alkenyl halides of the same structural type.



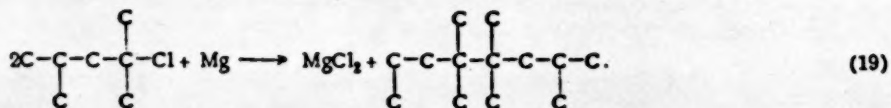
Somewhat lower yields were obtained when the isobutyl radical in the tertiary halide was replaced by propyl and, particularly, by ethyl (Equations 16 and 17):



At the same time, it was shown that the use of 2-methylallyl chloride in the condensation instead of allyl chloride results in some improvement in the yield, but the improvement is relatively small. The increase of the yields in a series of condensation products formed with allyl or 2-methylallyl chloride by halogen compounds in which a methyl standing at the central carbon, which is attached to the halogen, is replaced successively by ethyl, propyl and isobutyl is probably to be explained by the inductive effect on the carbon-halogen bond, which is known [11] to increase in the series:



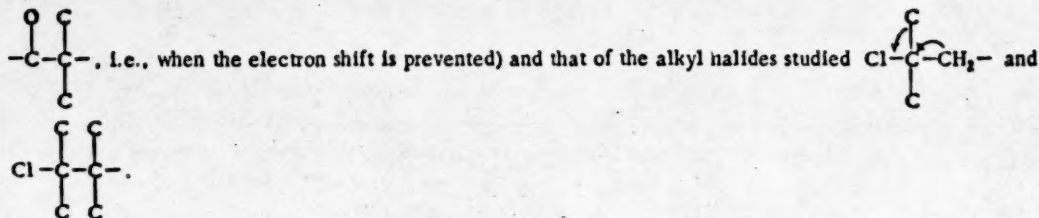
It is interesting also to note that the reaction of Equation 19 went with a yield of 6%, whereas hexamethyl-ethane is obtained in only 3% yield under these conditions, and octamethylhexane is not formed at all.





It is possible that the high yields obtained in the reactions of Equations 14, 15, 16 and 19 are to be attributed not only to the inductive effect, but also to  $\sigma, \sigma$ -conjugation, but in order to prove the existence of this effect further investigations are necessary. We may note, however, the parallelism existing between the reactivity of

ketones (high when the hydrogens on the  $\alpha$ -C are unsubstituted  $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{CH}_2- \\ | \\ \text{H} \end{array}$ , and low when they are substituted



## EXPERIMENTAL

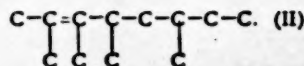
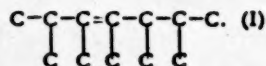
**2,3,4,5,6-Pentamethylheptane.** From 108 g of acetyl chloride and 98 g of 2-methyl-2-butene, 72 g of 3,4-dimethyl-3-penten-2-one (b.p. 146-147°,  $n_D^{20}$  1.4472;  $d_4^{20}$  0.8678) was prepared by Kondakov's method [12]. A mixture of the product (72 g) and 94 g of 3-chloro-2-methyl-1-butene as a solution in 300 ml of ether was added with stirring to 50 g of magnesium in 300 ml of ether. Stirring was continued for 70 hours without the application of heat, and decomposition was then effected with ammonium chloride solution and ice. Ether was distilled off at atmospheric pressure, and at reduced pressure the  $C_{10}$  diene fraction came over up to 65° (7 mm) and was followed by 56 g (48%) of a fraction boiling at 76-77° (7 mm) and having  $n_D^{20}$  1.4710 and  $d_4^{20}$  0.8833; this was the tertiary alcohol, 2,3,4,5,6-pentamethyl-1,5-pentadien-4-ol (or, if the allyl halide underwent isomerization, 2,3,4,6-tetramethyl-2,6-octadien-4-ol).

The alcohol (15 g) was oxidized with a 2% potassium permanganate solution. Among the neutral oxidation products, acetone (its 2,4-dinitrophenylhydrazone gave no depression with that of acetone) and 2,3-butanedione (2,4-dinitrophenylhydrazone, m.p. 314-315°) were identified. In the evaporated solution of salts only formic acid (no acetic) was detected, and it was determined quantitatively by the calomel method (1.1633 g). The isomeric 2,3,4,6-tetramethyl-2,6-octadien-4-ol should have yielded acetone, 2,3-butanedione, and acetic acid, so that our only evidence for the absence of this alcohol and, therefore, of the non-occurrence of the allyl rearrangement rests on the results of the investigation of the acid fraction. It is fortunate that we were able to obtain supplementary evidence in the course of later investigation for the absence of this alcohol (and, therefore, for the non-occurrence of the allyl rearrangement) in the products of the condensation of the allyl halide with the unsaturated ketone.

2,3,4,5,6-Pentamethyl-1,5-heptadien-4-ol (40 g) was boiled for 30 hours with 69 g of acetic anhydride and 27 g of sodium acetate. The products isolated were 15.3 g of a fraction boiling at 55-56° (7 mm) and having  $n_D^{20}$  1.4650 and  $d_4^{20}$  0.8118, which corresponded to the triene 2,3,4,5,6-pentamethyl-1,3,5-heptatriene, and 10.2 g of unchanged alcohol. The triene (15 g) was subjected to hydrogenation in methanol solution over Raney nickel at 169° and 120 atm. The hydrogenation product had the following properties: b.p. 60-68° (10 mm);  $n_D^{20}$  1.4418;  $d_4^{20}$  0.7862; it readily decolorized bromine water. The presence in the hydrogenation product of one double bond was confirmed also by Raman spectrum analysis and by elementary analysis.

	Found %:	C 85.25; H 14.69
$C_{12}H_{24}$	Calculated %:	C 85.63; H 14.37
$C_{12}H_{24}$	Calculated %:	C 84.61; H 15.39

In view of the fact that tetrasubstituted ethylenes are considerably more difficult to hydrogenate than disubstituted ethylenes, and also that the difficulty of hydrogenation increases when the double bond is moved to the center of the molecule, we supposed that the hydrogenation product was 2,3,4,5,6-pentamethyl-3-heptene (I) with some admixture of 2,3,4,6-tetramethyl-2-octene (II) (though only if at least partial allyl rearrangement had occurred)



In order to establish the structure of the olefin, it was subjected to permanganate oxidation. In the cold, oxidation proceeded with difficulty: the hydrocarbon was not oxidized even with a 6% solution of potassium permanganate. It was oxidized at the boil for ten days, and 4.7 g of the hydrocarbon gave the following neutral oxidation products (no acid oxidation products were detected):

Fraction 1, b.p. 77-98°: 0.2 g;  $n_D^{20}$  1.3881

Fraction II, b.p. 120-130°; 0.2 g;  $n_D^{20}$  1.4134

Fraction III, b.p. 62-65° (10 mm); 1.4 g;  $n_D^{20}$  1.4412

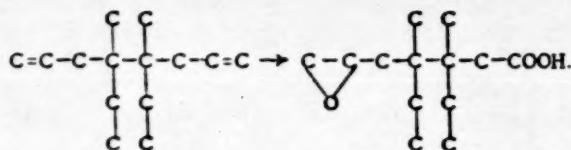
Fraction I gave a precipitate with 2,4-dinitrophenylhydrazine: the product melted at 116-117° after four recrystallizations and gave no depression in admixture with the 2,4-dinitrophenylhydrazone of 3-methyl-2-butanone. Fraction II gave a 2,4-dinitrophenylhydrazone of m.p. 101-102°, which corresponds [13] to the dinitrophenylhydrazone of 3,4-dimethyl-2-pentanone. The absence in the oxidation products of acetone and of a C<sub>9</sub> ketone may be taken as proof that there is no olefin (II) present in the olefin investigated. Fraction III was found to be unoxidized olefin. When a more active catalyst than nickel was used, namely palladium on silica gel, over which the olefin was treated at 163° and 124 atm, it was found possible to convert it into the paraffin hydrocarbon 2,3,4,5,6-pentamethylheptane, b.p. 64-66° (11 mm);  $n_D^{20}$  1.4392;  $d_4^{20}$  0.7838; freezing point below -80° (freezes to a glass).

4,5-Diethyl-4,5-dimethyloctane. An ethereal solution of 100 g of 3,4-dichloro-3,4-dimethylhexane and 152 g of allyl chloride was added dropwise to 48 g of magnesium. At the beginning of the addition the small amount of chloro compounds present was heated to the boiling point of ether, but when the reaction began the water bath was replaced by an acetone bath in which a temperature of  $-20^{\circ}$  was maintained throughout the addition operation. After decomposition of the reaction product and removal of ether, two fractions were separated by fractional distillation:

Fraction 1, b.p. 178-180° (760 mm); yield 38%;  $n_D^{20}$  1.4560;  $d_4^{20}$  0.802,

Fraction II, b.p. 210-215° (760 mm); yield 10%;  $n_D^{20}$  1.4620;  $d_4^{20}$  0.818.

When Fraction II was oxidized with a 1% solution of potassium permanganate, only acid oxidation products were obtained. Among these formic acid was identified, and fractional precipitation with silver nitrate gave the silver salt of an acid containing 31.82% Ag. For the salt of an epoxy acid  $C_{11}H_{22}O_3Ag$  the percentage of silver would be 32.2. The epoxy acid was evidently formed according to the scheme:



The fraction of b.p. 210-215° was hydrogenated over Raney nickel at 190° and 200 atm. The hydrogenation product boiled at 216-218°, had a freezing point of below -80°, and had  $n_D^{20}$  1.4440, and  $d_4^{20}$  0.798.

**4-tert-Butyl-2,4,6-trimethylheptane.** The reactants were magnesium (73 g), pinacolone (100.3 g), and 2-methylallyl chloride (135 g). The reaction was carried out in accordance with Yarovsky's procedure. The product was 142 g of 2,2,3,5-tetramethyl-4-hexen-3-ol, b.p. 46° (4 mm);  $n_D^{20}$  1.4502;  $d_4^{20}$  0.8514. Whitmore [14] has previously prepared an alcohol of this structure, but by another method (reaction of mesityl oxide with tert-butylmagnesium chloride) and in considerably lower yield, and he reported very similar physical properties. The structure of the alcohol, which, on account of the displacement of the double bond, was 2,2,3,5-tetramethyl-4-hexen-3-ol.

was proved by oxidation, the identified products being acetone and the crystalline hydroxy acid  $\begin{array}{c} \text{C} \quad \text{OH} \\ | \quad | \\ \text{C}-\text{C}-\text{C}-\text{COOH} \\ | \quad | \\ \text{C} \quad \text{C} \end{array}$ .

m.p. 141°, previously described by Petrov and Lavrishcheva [10]. A mixture test with the previously synthesized acid showed no depression. As a result of an attempt to carry out the hydrochlorination of this unsaturated acid, the dichloro compound  $C_{10}H_{20}Cl_2$  was obtained. The unsaturated alcohol was then hydrogenated, and the product had the following properties: b.p. 84.6-84.8° (25 mm);  $n_D^{20}$  1.4368;  $d_4^{20}$  0.8393. The conversion of 2,2,3,5-tetramethyl-3-hexanol into its hydrochloric ester was carried out by the passage of HCl at 0°. The chlorocompound

boiled at 72.6–73.5° (28 mm) and had  $n_D^{20}$  1.4455 and  $d_4^{20}$  1.8778. This chloro compound was condensed with 2-methylallyl chloride by Yarovsky's method. The condensation product had the following properties: b.p. 92.5° (12 mm);  $n_D^{20}$  1.4584;  $d_4^{20}$  0.8163; its hydrogen product had  $d_4^{20}$  0.7995, and its freezing point was –86°.

**3-Ethyl-2,2,3-trimethylhexane.** The materials taken for the reaction were 28 g of magnesium, 500 ml of absolute ether, 76.6 g of allyl chloride, and 124.2 g of 3-chloro-2,2,3-trimethylpentane [4]. The reaction was carried out by Yarovsky's procedure, the mixture of chloro compounds being added over six hours. The contents of the flask were then heated for 36 hours, and decomposition was effected with 5% HCl. After removal of ether, the residue was fractionated through a column over sodium, and 11 g (9%) of 4-ethyl-4,5,5-trimethyl-1-hexene (b.p. 59° (12 mm);  $n_D^{20}$  1.4403;  $d_4^{20}$  0.7834) was obtained. The olefin was hydrogenated over Raney nickel at 140°, the initial pressure being 130 atm. The hydrogenation product, after distillation through a column, had the following properties: b.p. 176.5° (739 mm);  $n_D^{20}$  1.4386;  $d_4^{20}$  0.7783; freezing point –110° (it freezes to a glass).

**2,4,4,5,5,7-Hexamethyloctane.** 2,4-Dimethyl-2-pentanol was prepared by Konovalov's method [15]. The corresponding chloro compound was then synthesized for the first time by treatment with gaseous HCl at 0°. The yield was 70%, and it had b.p. 52° (46 mm);  $n_D^{20}$  1.4180;  $d_4^{20}$  0.8601.

Found %: Cl 26.72  
 $C_{11}H_{22}Cl$ . Calculated %: Cl 26.33

The materials taken for the reaction were 11 g of magnesium, 500 ml of absolute ether, and 125.9 g of 2-chloro-2,4-dimethylpentane. Reaction was initiated by the addition of 2 ml of ethyl bromide, and a solution of the chloro compound in ether was then added over six hours. After the addition was complete the contents of the flask were heated at the boiling point of ether for 32 hours. After removal of ether and 2,4-dimethyl-1-pentene by distillation, the residue was fractionated over sodium through a six-plate column. The product was 5.2 g (6%) of 2,4,4,5,5,7-hexamethyloctane, b.p. 216° (743 mm);  $n_D^{20}$  1.4408;  $d_4^{20}$  0.7902; freezing point +2° (crystals).

Yu. P. Egorov determined the Raman spectrum of the hydrocarbon, which included intensive lines at 697, 936, 1210, and 1236  $cm^{-1}$ . A consideration of Stepanov's calculations [16] and experimental data for  $C_{10}$ – $C_{12}$  hydrocarbons having tertiary carbons at the periphery and at the center shows that these lines must be regarded as characterizing the presence of two tertiary carbons in the center of the molecule. The frequencies 823, 960, and 1173  $cm^{-1}$ , characterizing simple branching at the end of the chain, were also found in the spectrum.

It is interesting to note that, as Levina [17] has shown, it is not possible to obtain the above-indicated structure (but in the form of a diolefin) by the condensation of two molecules of the HBr-addition product from 2,4-dimethyl-1,3-pentadiene in presence of sodium; quantitative dehydrobromination to 2,4-dimethyl-1,3-pentadiene occurs, and a dimer of composition  $C_{12}H_{24}$  is formed.

## SUMMARY

1. It is shown that the use of 2-alkenyl halides or ketones having a  $\alpha,\beta$ -double bond in organomagnesium syntheses gives higher yields than those obtained with saturated halogen compounds or ketones and, moreover, permits the synthesis of compounds that are so greatly branched that they cannot be obtained at all when saturated components are used in the synthesis.

2. Halogen compounds of the allyl type that are able to undergo the allyl rearrangement during condensation with saturated ketones do not undergo this change during condensation with  $\alpha,\beta$ -unsaturated ketones (i.e., when there is a conjugated system of bonds in each component).

3. Whereas the condensation of allyl and 2-methylallyl halides with symmetrical saturated tertiary halides containing two adjacent quaternary carbons (2-halo-2,3,3-trimethylbutane) proceeds with low yield, asymmetrical halogen compounds of the same type but of higher molecular weight, in which one of the methyl radicals standing at the carbon attached to the halogen is replaced by propyl or isobutyl, give high yields in the condensation reaction.

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\* T p. = Consultants Bureau Translation pagination.



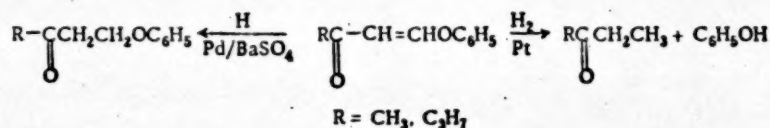
## SOME REACTIONS OF ALKYL 2-PHENOXYVINYL KETONES

A. N. Nesmeyanov, N. K. Kochetkov, M. I. Rybinskaya and E. V. Uglova

Alkyl 2-phenoxyvinyl ketones, which were prepared recently in our laboratory by the reaction of alkyl 2-chlorovinyl ketones with phenols [1], have received very little study. The readiness with which the phenoxy group undergoes exchange reactions is of interest: it is eliminated in treatments with acidic reagents and also in the formation of heterocyclic systems from 2-phenoxyvinyl ketones [1]. Apart from these reactions we have studied a peculiar rearrangement of 2-phenoxyvinyl ketones into pyrylium salts which is reminiscent of the Fries rearrangement [2].

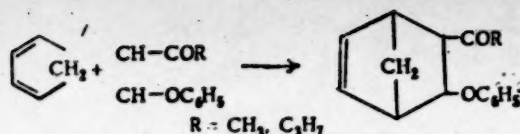
The present paper is devoted to the further investigation of the chemical behavior of alkyl 2-phenoxyvinyl ketones. It was considered to be of interest to compare the reactivity of these substances with that of 2-dialkylaminovinyl ketones, which have been recently studied by one of us [3], and also with that of 2-chlorovinyl ketones. It would be expected that, with respect to the activity of the double bond and carbonyl group, 2-phenoxyvinyl ketones would occupy an intermediate position between these other two classes of compound. The conjugation of the free electron pair of the hetero-atom with the double bond and the carbonyl group, to which the deactivation found in aminovinyl ketones is to be attributed  $\text{R}-\text{C}(\text{O})=\text{CH}=\text{CH}-\text{NR}_2$  [3], will obviously be less effective when nitrogen is replaced by the oxygen of the phenoxy group, though in the phenoxyvinyl ketones this conjugation must be more marked than in 2-chlorovinyl ketones. These considerations lead us to suppose that in 2-phenoxyvinyl ketones the carbonyl group and, particularly, the double bond will be less reactive than in 2-chlorovinyl ketones, though this deactivation will not be as great as in 2-dialkylaminovinyl ketones. Our results confirm this view.

We first examined the catalytic hydrogenation of alkyl 2-phenoxyvinyl ketones at room temperature and normal pressure with the object of comparing them with 2-aminovinyl ketones, which are unable to undergo normal hydrogenation [3]. It was found that the hydrogenation of alkyl 2-phenoxyvinyl ketones (the methyl and propyl ketones were used) takes different courses according to which catalyst is used. Over palladium precipitated on barium sulfate the reaction goes normally, and the corresponding alkyl 2-phenoxyethyl ketones are formed in high yield, although it must be pointed out that the process is very slow, the hydrogenation of even very small amounts being complete only after 6-7 hours. On the other hand, hydrogenation over an Adams platinum catalyst does not give the expected reaction product. Instead, hydrogenolysis of the oxygen-carbon bond occurs, and only phenol and the corresponding saturated ketone can be isolated from the reaction mixture:



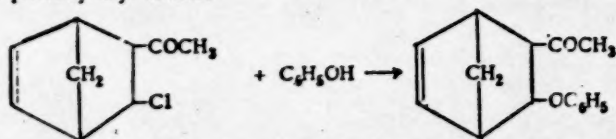
The hydrogenation of alkyl 2-phenoxyvinyl ketones is, therefore, an example of a reaction in which catalysts as similar in character as platinum and palladium give completely different results. The observed behavior shows also that in alkyl 2-phenoxyvinyl ketones the double bond is indeed deactivated (slow hydrogenation over palladium; hydrogenolysis over platinum). This deactivation, however, is not as great as that found in 2-aminovinyl ketones, since the latter, unlike the phenoxy compounds, are unable to undergo normal hydrogenation.

From this point of view the observed behavior of alkyl 2-phenoxyvinyl ketones in a diene-synthesis reaction is particularly characteristic. It is known that 2-chlorovinyl ketones are active dienophiles [4, 5], whereas, owing to the complete deactivation of the double bond, 2-dialkylaminovinyl ketones do not condense with dienes [3]. It was found that neither at room temperature nor at 100° for several hours will methyl or propyl 2-phenoxyvinyl ketone condense with cyclopentadiene, which was selected as one of the most active dienes. This behavior sharply differentiates 2-phenoxyvinyl ketones from 2-chlorovinyl ketones, which react already in the cold with cyclopentadiene [4], forming adducts in high yield. However, under very vigorous conditions (145-155° for 15-16 hours) normal diene condensation occurs with formation of the corresponding phenoxy derivatives of bicyclo[2.2.1]hept-2-ene:



It must be pointed out, however, that under the severe conditions the condensation products are formed in moderate yields (30-50%). The structures of the resulting compounds were confirmed by tests for the double bond and the carbonyl group (formation of a dinitrophenylhydrazone) and by a positive Iodoform test.

A confirmatory synthesis was carried out for 5-acetyl-6-phenoxybicyclo[2.2.1]hept-2-ene (methyl 3-phenoxybicyclo[2.2.1]hept-5-en-2-yl ketone), the starting point being 5-acetyl-6-chlorobicyclo[2.2.1]hept-2-ene, which has been prepared previously [4]. As one of us and Karpelsky [6] have shown, the chlorine atom of this compound can readily be replaced by other nucleophilic groups. We found that treatment of 5-acetyl-6-chlorobicyclo[2.2.1]hept-2-ene with sodium phenoxide in molten phenol or with phenol in an aqueous medium gave a phenoxy derivative in high yield, and the product was found to be identical with the substance obtained by the direct condensation of cyclopentadiene and methyl 2-phenoxyvinyl ketone:

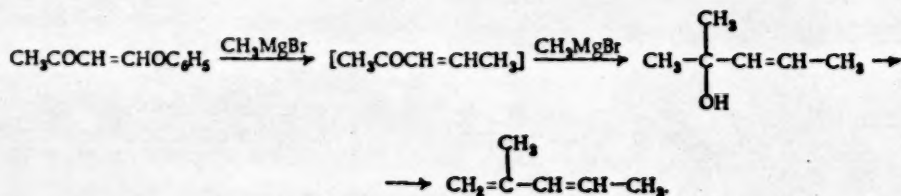


The results obtained for the reaction of the chlorobicyclo[2.2.1]hept-2-ene with phenol are interesting in that they provide final confirmation for the hypothesis advanced previously [6], according to which the replacement of chlorine in this compound occurs without Wagner rearrangement of the carbon skeleton.

Reverting now to the diene condensation of 2-phenoxyvinyl ketones, we must conclude that the results obtained provide particularly clear evidence for the middle place that the double bond of 2-phenoxyvinyl ketones occupies, with respect to activity, in the series: 2-chlorovinyl ketones - 2-phenoxyvinyl ketones - 2-aminovinyl ketones.

In order to elucidate the nature of the carbonyl group in alkyl 2-phenoxyvinyl ketones, it was of interest to determine the behavior of these compounds in reaction with organomagnesium compounds. Investigation showed that reactions of this type are rather complex, and this paper describes only the reaction of methyl 2-phenoxyvinyl ketone with methylmagnesium bromide. Carrying out the reaction under the usual conditions, i.e., by addition of methyl 2-phenoxyvinyl ketone to an equimolecular amount of the organomagnesium compound, we were able to isolate two substances from the reaction mixture, the total yield being about 20%. One of these substances was the unsaturated alcohol 2-methyl-3-penten-2-ol, and the other the product resulting from the dehydration of this alcohol - 2-methyl-1,3-pentadiene. The structure of the latter was proved not only by the coincidence of constants, but also by the preparation of its previously known adduct with maleic anhydride. The structure of the alcohol was confirmed by its conversion into the same 2-methyl-1,3-pentadiene by dehydration in presence of small amounts of sulfuric acid. The combined yield of alcohol and diene was increased when excess of the organomagnesium compound was used; it attained 40% when 100% excess was used, and at the same time the relative proportion of diene in the mixture increased [7]. The same results were obtained by carrying out the reaction under different conditions - under intense cooling (to  $-50^\circ$ ) and with reversal of the order of mixing the reactants - but the yields of diene and alcohol were then reduced.

The formation of 2-methyl-3-penten-2-ol, and hence of the diene obtained by its dehydration, can be most readily understood on the assumption that the unsaturated ketone 3-penten-2-one is first formed and then reacts further with the organomagnesium compound to give the unsaturated alcohol:



Hence, the first stage of the reaction is probably the replacement of the phenoxy group, and not condensation at the carbonyl group. We cannot maintain that this is the only direction that reaction takes, for the yield of the

Isolated substances is only 40% and the residue remaining undistilled is considerable and may contain substances formed by primary reaction at the carbonyl group. It is notable also that 2-chlorovinyl ketones react only at the carbonyl group with organomagnesium compounds [8]. However, the primary reaction of the phenoxyvinyl ketones is replacement of the phenoxy group, which indicates some suppression of the typical properties of the carbonyl group relative to the level found in 2-chlorovinyl ketones.

Thus, the results of catalytic hydrogenation, diene condensation, and reaction with organomagnesium compounds confirm the correctness of the hypothesis advanced at the beginning of the paper concerning the middle place occupied by 2-phenoxyvinyl ketones in the series: 2-chlorovinyl ketones — 2-phenoxyvinyl ketones — 2-aminovinyl ketones.

Finally, we investigated the peculiar reaction of hydrolytic decomposition which 2-phenoxyvinyl ketones undergo in an alkaline medium. It was found that these substances are in no sense inert to the action of aqueous alkalis, a fact which had been indicated indirectly in the course of the development of the method for synthesizing them [1]. When methyl 2-phenoxyvinyl ketone was heated at 30–40° for several hours with 15% aqueous caustic soda, hydrolytic decomposition occurred; acetone and phenol were isolated from the resulting mixture and identified, and a calomel test indicated the presence of formic acid. Similar hydrolytic decomposition is undergone by certain alkoxyvinyl ketones [9]. The occurrence of such decomposition indicates the peculiar character of alkyl phenoxyvinyl ketones, which can be regarded as vinyls of phenyl esters.

## EXPERIMENTAL

1. Hydrogenation of methyl 2-phenoxyvinyl ketone (4-phenoxy-3-buten-2-one) over palladium. Methyl 2-phenoxyvinyl ketone (9.0 g) was hydrogenated in 80 ml of absolute ether over palladium precipitated on barium sulfate (0.5 g of catalyst containing 7% of palladium). In the course of six hours 1.09 liters of hydrogen (calculation requires 1.24 liters) was absorbed, and hydrogenation was discontinued. The catalyst was filtered off, and the filtrate was washed with an alkaline permanganate solution, washed with water, and dried over sodium sulfate. The ether was removed, and the residue was vacuum-distilled. After redistillation methyl 2-phenoxyethyl ketone had the following constants: b.p. 123–124° (8 mm);  $d_4^{20}$  1.0606;  $n_D^{20}$  1.5165; yield 6.6 g (73.3%).

Found %: C 73.24; 73.04; H 7.38; 7.29

$C_{10}H_{12}O_2$ . Calculated %: C 73.14; H 7.37

Methyl 2-phenoxyethyl ketone (4-phenoxy-2-butanone) is a colorless liquid of pleasant odor. It is immiscible with water.

Its dinitrophenylhydrazone was prepared in the usual way. After recrystallization from alcohol it was obtained as yellow needles melting at 143–144°.

Found %: N 16.38; 16.39

$C_{16}H_{16}O_5N_4$ . Calculated %: N 16.28

Its oxime was prepared in the usual way. After recrystallization from alcohol it was obtained as colorless needles melting at 67–68°.

Found %: N 8.07; 7.85

$C_{10}H_{13}O_2N$ . Calculated %: N 7.82

2. Hydrogenation of 2-phenoxyvinyl propyl ketone (1-phenoxy-1-hexen-3-one) over palladium. The hydrogenation of 7.0 g of 2-phenoxyvinyl propyl ketone was carried out in a similar way (0.4 g of catalyst). In the course of 6.5 hours, 800 ml of hydrogen was absorbed (theory requires 820 ml). Similar treatment yielded 5.0 g (71.4%) of 2-phenoxyethyl propyl ketone, b.p. 126–126.5° (4 mm), which solidified completely. After recrystallization from petroleum ether the substance melted at 36–37.5°.

Found %: C 75.35; 75.36; H 8.32; 8.26

$C_{12}H_{16}O_2$ . Calculated %: C 75.00; H 8.39

2-Phenoxyethyl propyl ketone (1-phenoxy-3-hexanone) is soluble in alcohol and ether, but not in water.

3. Hydrogenation of 2-phenoxyvinyl propyl ketone over platinum. 2-Phenoxyvinyl propyl ketone (10.0 g) was hydrogenated in 70 ml of absolute ether over 0.2 g of Adams platinum oxide. In the course of ten hours 2.20 liters of hydrogen was absorbed (theory requires 2.30 liters for two molecular proportions). The catalyst was filtered off, and the filtrate was washed with 10% caustic soda solution, washed with an alkaline permanganate solution, and



dried over sodium sulfate. The residue remaining after removal of ether was distilled twice, and a fraction boiling at 120-125° was collected. This fraction was converted into its dinitrophenylhydrazone, which was recrystallized from alcohol as yellow crystals, m.p. 128-129°. It showed no depression in melting point when mixed with the dinitrophenylhydrazone of ethyl propyl ketone (3-hexanone), the reported melting point of which is 130° [10]. The aqueous-alkali extract was acidified with 20% sulfuric acid, and bromine water was added until it was no longer decolorized. The precipitate of tribromophenol was filtered off and recrystallized from alcohol in the form of colorless crystals, m.p. 92-93°, undepressed by admixture of a known sample. The reported melting point of tribromophenol is 94° [11].

4. Condensation of methyl 2-phenoxyvinyl ketone with cyclopentadiene. A mixture of 10 g of methyl 2-phenoxyvinyl ketone and 6.5 g of freshly distilled cyclopentadiene was prepared in an ampoule, which was placed, unsealed, in a small autoclave and heated at 145-155° for 15 hours. The reaction products from three such experiments were combined and vacuum-distilled, the fraction boiling at 132-138° (1.5 mm) being collected. After redistillation, 5-acetyl-6-phenoxybicyclo[2.2.1]hept-2-ene had the following constants: b.p. 132-134° (1.5 mm);  $d_4^{20}$  1.1159;  $n_D^{20}$  1.5481; found MR 64.93; calculated for  $C_{15}H_{16}O_2$   $\bar{M}$ : MR 64.65; the yield was 13.6 g (29%).

Found %: C 78.61; 78.50; H 7.17; 7.06  
 $C_{15}H_{16}O_2$  Calculated %: C 78.94; H 7.01

The substance is a yellowish viscous oil having a camphorlike odor. It changes little with keeping.

Its dinitrophenylhydrazone was prepared in the usual way. After recrystallization from glacial acetic acid it formed orange needles, m.p. 152-153°.

Found %: C 62.65; H 5.05  
 $C_{21}H_{20}O_4N_4$  Calculated %: C 61.72; H 4.90

5. Condensation of 2-phenoxyvinyl propyl ketone with cyclopentadiene. The reaction was carried out under similar conditions with 12 g of 2-phenoxyvinyl propyl ketone and 10 g of cyclopentadiene, two experiments being performed. After two redistillations, 5-butyryl-6-phenoxybicyclo[2.2.1]hept-2-ene had the following constants: b.p. 147-150° (2 mm);  $d_4^{20}$  1.0814;  $n_D^{20}$  1.5370; found MR 73.89; calculated for  $C_{17}H_{20}O_2$   $\bar{M}$ : MR 73.89; the yield was 15.9 g (49%).

Found %: C 79.56; 79.45; H 7.90; 7.97  
 $C_{17}H_{20}O_2$  Calculated %: C 79.61; H 7.87

The substance is a yellowish viscous oil having a camphorlike odor. It changes little with keeping.

6. Reaction of 5-acetyl-6-chlorobicyclo[2.2.1]hept-2-ene with phenol. A. To 75 g of melted phenol 1.35 g of sodium was added in small portions, and then 10 g of 5-acetyl-6-chlorobicyclo[2.2.1]hept-2-ene [4] was added gradually. The mixture was shaken for 5.5 hours, heat being applied from time to time. It was then poured into water, and 75 ml of 40% caustic soda was added. The mixture was filtered, and the filtrate was extracted with ether. The extract was washed with 10% caustic soda to remove phenol, and then washed with water and dried over sodium sulfate. Ether was distilled off, and the residue was vacuum-distilled. 5-Acetyl-6-phenoxybicyclo[2.2.1]hept-2-ene has the following constants: b.p. 136-140° (5 mm);  $d_4^{20}$  1.1157;  $n_D^{20}$  1.5471; the yield was 6.45 g (48.9%).

B. 5-Acetyl-6-chlorobicyclo[2.2.1]hept-2-ene (10 g) was added to a solution of 25 g of phenol in 45 ml of 40% caustic potash solution, the mixture being shaken during the addition and then for a further five hours. After the treatment described above (A), 9.6 g (72.2%) of 5-acetyl-6-phenoxybicyclo[2.2.1]hept-2-ene was obtained. It had the following properties: 136-138° (5 mm);  $d_4^{20}$  1.1161;  $n_D^{20}$  1.5477.

The dinitrophenylhydrazones obtained in the usual way from the two samples of 5-acetyl-6-phenoxybicyclo[2.2.1]hept-2-ene both melted at 152-154° after recrystallization from acetic acid. Mixture tests on these two samples and the sample obtained in Experiment 4, taken in pairs, showed no depression.

7. Reaction of methyl 2-phenoxyvinyl ketone with methylmagnesium bromide. A solution of methylmagnesium bromide was prepared in the usual way from 16 g of magnesium and the corresponding amount of methyl bromide in 350 ml of ether. It was placed in a three-necked flask, which was provided with stirrer, reflux condenser, and dropping funnel. Cooling was applied by means of an ice mixture, and 50 ml of a solution of 50 g of methyl 2-phenoxyvinyl ketone in 75 ml of ether was added dropwise. Toward the end of the reaction a white precipitate appeared. The mixture was stirred for one hour and then poured into a mixture of ice and ammonium chloride. The ether layer was separated, and the aqueous layer was extracted with ether. The combined extract was washed with 3% caustic soda solution to remove phenol, and was then washed with water and dried over sodium



sulfate. The ether was carefully distilled off, and the residue was distilled. At 82-90° a substance came over together with water. The water was separated, and the organic layer was dried and redistilled, two fractions being collected: Fraction I, b.p. 74-77° (750 mm), and Fraction II, b.p. 68-72° (128 mm). Redistillation of Fraction I yielded 2-methyl-1,3-pentadiene, the constants of which were: b.p. 74-75° (750 mm);  $d_4^{20}$  0.7209;  $n_D^{20}$  1.4460; the yield was 5.2 g (20%). For 2-methyl-1,3-pentadiene the literature [12] gives b.p. 75.6-76°;  $d_4^{20}$  0.7190;  $n_D^{20}$  1.4466.

Found %: C 87.71; 87.69; H 12.46; 12.31  
 $C_6H_{10}$  Calculated %: C 87.80; H 12.20

Redistillation of Fraction II yielded 2-methyl-3-penten-2-ol, which had the following constants: b.p. 121-122°;  $d_4^{20}$  0.8370;  $n_D^{20}$  1.4302; The yield was 6.1 g (19%). For 2-methyl-3-penten-2-ol the literature [12] gives b.p. 121.6-122°;  $d_4^{20}$  1.4295;  $n_D^{20}$  0.8343.

Found %: C 71.62; 71.47; H 12.13; 11.97  
 $C_6H_{12}O$  Calculated %: C 71.95; H 12.01

After the distillation of Fractions I and II, a thick resinous mass remained in the distillation flask, and from this we could remove only a small amount of phenol by distillation.

8. Reaction of 2-methyl-1,3-pentadiene with maleic anhydride. A mixture of 1.6 g of the diene, 1.9 g of maleic anhydride, and 25 ml of benzene was set aside overnight. Benzene was then removed under reduced pressure, and the residue was washed with hot water. The undissolved crystals were filtered off and recrystallized from ligroin. Colorless plates melting at 55.5-56.5° were obtained. For the adduct formed by 2-methyl-1,3-pentadiene with maleic anhydride the literature [13] gives m.p. 57°.

9. Dehydration of 2-methyl-3-penten-2-ol. A few drops of 40% sulfuric acid were added to 7 g of the alcohol contained in a Favorsky flask, and the mixture was heated gently over a gauze. The distillate separated into two layers, and the water layer was removed. The organic layer was dried over sodium sulfate and distilled, when it yielded 4.7 g (84%) of 2-methyl-1,3-pentadiene, b.p. 75-77°;  $d_4^{20}$  0.7207;  $n_D^{20}$  1.4460.

The adduct with maleic anhydride, prepared as described above, melted at 55-56° and showed no depression of melting point in admixture with the substance obtained in Experiment 8.

10. Reaction of methyl 2-phenoxyvinyl ketone with alkali. Methyl 2-phenoxyvinyl ketone (28 g) was stirred vigorously for 4-5 hours with 170 ml of a 15% solution of caustic soda, the mixture being heated in a water bath maintained at 40-50°. At the end of the reaction the mixture became homogeneous. A fraction boiling at 53-58° was separated from it with the aid of a good fractionating column. After redistillation the substance boiled at 55-57°. It was converted in the usual way into its dinitrophenylhydrazone, which had m.p. 122°, undepressed by admixture of known dinitrophenylhydrazone of acetone, for which the literature [14] gives m.p. 122-124°.

The residue remaining after removal of acetone was acidified with 10% sulfuric acid until feebly acid to litmus, and was then saturated with sodium carbonate. The solution was extracted with ether, the extract was dried over sodium sulfate, and the ether was distilled off. Distillation of the residue yielded 12.8 g (78.7%) of phenol, which was identified by conversion into tribromophenol. To one twenty-fifth part of the alkaline solution a saturated mercuric chloride solution was added. The mixture was brought to the boil and then set aside overnight. The precipitate of calomel was filtered off. The yield was 1.45 g, which corresponds to 0.25 g (80% of the theoretical amount) of formic acid. An ammonia test for calomel was positive.

## SUMMARY

1. Hydrogenation of alkyl 2-phenoxyvinyl ketones over a palladium catalyst yields alkyl 2-phenoxyethyl ketones, but in their hydrogenation over a platinum catalyst hydrogenolysis of the carbon-oxygen bond occurs, so that phenol and the corresponding saturated ketone are formed.
2. Reaction of alkyl 2-phenoxyvinyl ketones with cyclopentadiene yields derivatives of bicyclo[2.2.1]hept-2-ene. This reaction, however, goes only under severe conditions, and the yields are not high.
3. Reaction of methyl 2-phenoxyvinyl ketone with methylmagnesium bromide results in the formation of 2-methyl-1,3-pentadiene and 2-methyl-3-penten-2-ol.
4. When methyl 2-phenoxyvinyl ketone is heated with aqueous alkali, it undergoes hydrolytic decomposition to acetone, phenol and formic acid.
5. The results indicate that, with respect to the reactivities of the double bond and carbonyl group, 2-phenoxyvinyl ketones occupy an intermediate position between 2-chlorovinyl ketones and 2-aminovinyl ketones.

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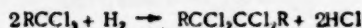
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\* T.p. = Consultants Bureau Translation pagination.

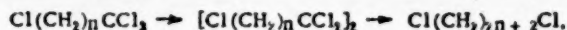
# SYNTHESIS OF DODECANEDIOIC AND HEXADECANEDIOIC ACIDS

A. N. Nesmeyanov, L. I. Zakharkin and T. A. Kost

$\alpha, \alpha, \omega$ -Tetrachloroalkanes  $\text{Cl}(\text{CH}_2)_n\text{CCl}_3$  are of interest for the synthesis of  $\alpha, \omega$ -bifunctional compounds on account of the possibility of applying the reductive dimerization reaction given by the  $\text{CCl}_3$  group:



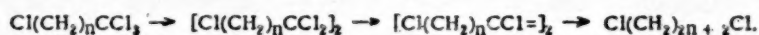
and of then reducing the  $\text{CCl}_2\text{CCl}_2$  grouping. The reductive dimerization of the  $\text{CCl}_3$  group has been studied in detail for benzotrichloride [1] and 2,2-diaryl-1,1,1-trichloroethanes [2, 3, 4]. For the preparation of compounds of this type reduction has been effected electrochemically, by the action of reducing agents of the Devarda type, and catalytically with Pt and Pd catalysts in presence of bases. The reductive dimerization of  $\alpha, \alpha, \omega$ -tetrachloroalkanes over a platinum catalyst (prepared from  $\text{PtO}_2$ ) in presence of ammonia is described in a patent [5], and it is stated that reduction can be carried out further with the formation of dimeric  $\alpha, \omega$ -dichloroalkanes:



The selective action of hydrogen in this reaction, in which it preferentially attacks a  $\text{CCl}_3$  group in presence of a  $\text{CH}_2\text{Cl}$  group, is in accord with the view that we have advanced previously, namely that the action of reagents of the radical type on tetrachloroalkanes should be directed, in the first place, to the  $\text{CCl}_3$  group [6].\*

The ready accessibility of 1,1,1,5-tetrachloropentane and 1,1,1,7-tetrachloroheptane makes it possible to use the compounds obtained by this reaction for the synthesis of the comparatively difficultly accessible dodecanedioic and hexadecanedioic acids. With this object we have made a more detailed investigation of the reductive dimerization of 1,1,1,5-tetrachloropentane and 1,1,1,7-tetrachloroheptane and of the further reduction of the products.

The reduction of tetrachloroalkanes to  $\alpha, \omega$ -dichloroalkanes proceeds in stages: after the formation of a dimeric hexachloroalkane, dechlorination occurs with formation of a dimeric tetrachloroalkene, which is then reduced to the  $\alpha, \omega$ -dichloroalkane:



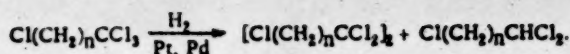
An interesting feature is the great ease with which the grouping  $-\text{CCl}=\text{CCl}-$  reduces, as compared with  $\text{CH}_2\text{Cl}$ .

Hence, by the reduction of 1,1,1,5-tetrachloropentane, 1,5,5,6,6,10-hexachlorodecane, 1,5,6,10-tetrachloro-5-decene, and 1,10-dichlorodecane can be prepared, and by the reduction of 1,1,1,7-tetrachloroheptane, 1,7,7,8,8,14-hexachlorotetradecane, 1,7,8,14-tetrachloro-7-tetradecene, and 1,14-dichlorotetradecane can be prepared.

We have observed also another example of dechlorination during the catalytic hydrogenation of such polychloro compounds: in the hydrogenation of 1,1,1,2,5-pentachloropentane there is no dimerization with formation of  $[\text{Cl}(\text{CH}_2)_3\text{CHClCCl}_2]_2$ , but dechlorination occurs with formation of 1,1,5-trichloro-1-pentene.

When 1,1,1,5-tetrachloropentane and 1,1,1,7-tetrachloroheptane are hydrogenated over a platinum catalyst (prepared from  $\text{PtO}_2$ ) or 5% Pd/BaSO<sub>4</sub> in presence of one equivalent of ammonia, similar results are obtained: hexachlorodecane and hexachlorotetradecane are obtained in yields varying around 50%, and at the same time considerable amounts of 1,1,5-trichloropentane and 1,1,7-trichloroheptane are obtained, i.e., hydrogenation proceeds in both possible directions:

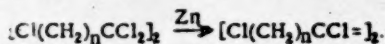
\* In this connection attention must be drawn to the incorrectness of a statement made in an American patent [7], namely that 1,1,1,6,6,6-hexachlorohexane results from the action of certain metals on 1,1,1,3-tetrachloropropane. The constants of this compound coincide with those of 1,3,3,4,4,6-hexachlorohexane, which we prepared by the action of Raney nickel on 1,1,3-tetrachloropropane.



$$n = 4 \text{ or } 6$$

When tetrachloropentane and tetrachloroheptane are hydrogenated in presence of two equivalents of ammonia, tetrachlorodecene and tetrachlorotetradecene, respectively, are obtained in 40-45% yield. The direct hydrogenation of tetrachloropentane and tetrachloroheptane to the corresponding  $\alpha, \omega$ -dichloroalkanes without the isolation of intermediate products proceeds very slowly in the last stage and does not go to completion. Hydrogenation of tetrachloropentane with Raney nickel in presence of aqueous or alcoholic ammonia at atmospheric pressure gives hexachlorodecane in a yield of only 7-9%, but when the reaction is carried out in presence of aqueous alkali at 60-80° the yield of hexachlorodecane is increased to 25-30%. When tetrachloropentane is hydrogenated over Raney nickel in presence of pyridine at 100 atm, no hexachlorodecane is formed, the main product being 1,1,5-trichloropentane. When tetrachloropentane is heated in alcoholic solution with a large amount of Raney nickel without passage of hydrogen, hexachlorodecane is formed.

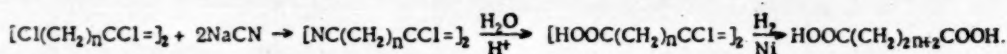
The hydrogenation of hexachlorodecane and of hexachlorotetradecane over Pt and Pd catalysts in presence of two molecular equivalents of ammonia proceeds readily, and tetrachlorodecene and tetrachlorotetradecene are formed in high yield. Both of the latter compounds are readily formed from the corresponding hexachloroalkanes when these are treated with zinc dust in alcoholic solution:



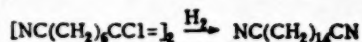
The structure of 1,5,6,10-tetrachloro-5-decene was confirmed by its ozonization to 5-chlorovaleric acid.

The hydrogenation of hexachlorodecane to 1,10-dichlorodecane over a Pt catalyst in presence of ammonia is very slow, and the reaction products include a large amount of tetrachlorodecene. Under these conditions, tetrachlorodecene and tetrachlorotetradecene are also hydrogenated very slowly. The hydrogenation of hexachloroalkanes and tetrachloroalkenes to  $\alpha, \omega$ -dichloroalkanes over Pd/BaSO<sub>4</sub> in presence of ammonia or diethylamine proceeds comparatively rapidly and in high yield.

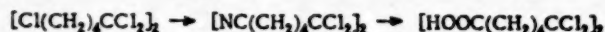
The hydrogenation of hexachlorodecane over Raney nickel in presence of diethylamine at high temperatures and pressures gives dichlorodecane in 70% yield; with ammonia the reaction goes poorly. It follows from our results that for the synthesis of dichlorodecane or dichlorotetradecane from the corresponding tetrachloroalkane the reduction must be carried out in two stages: first to a hexachloro or tetrachloro compound, and then the reduction of these to the  $\alpha, \omega$ -dichloroalkane. In view of the necessity for two-stage reduction, we consider that the best route for the synthesis of dodecanedioic and tetradecanedioic acids will be the following:



The reaction of sodium cyanide with tetrachlorodecene and with tetrachlorotetradecene proceeds smoothly in 2-ethoxyethanol solution; under the conditions of the reaction, the chlorine atoms at the double bond do not react with sodium cyanide. Nitriles obtained in this way were hydrolyzed by heating them with a mixture of hydrochloric and acetic acids, and the dicarboxylic acids formed were hydrogenated at high temperature and pressure in an aqueous alkaline medium in presence of Raney nickel, when dodecanedioic and hexadecanedioic acids were formed. 8,9-Dichloro-8-hexadecenedinitrile was reduced over Pd/BaSO<sub>4</sub> in presence of diethylamine and gave hexadecanedinitrile in good yield:



When hexachlorodecane was treated with sodium cyanide, only the terminal chlorine atoms reacted. The resulting 6,6,7,7-tetrachlorododecanedinitrile was hydrolyzed into the corresponding tetrachloro acid:



The corresponding nitriles were prepared also from 1,10-dichlorodecane and 1,14-dichlorotetradecane, and it was found that excellent results were obtained when 2-ethoxyethanol was used as solvent.



## EXPERIMENTAL

### Hydrogenation of 1,1,1,5-Tetrachloropentane to 1,5,5,6,6,10-Hexachlorodecane

a) 1,1,1,5-Tetrachloropentane (500 g) and 794 ml of a solution of ammonia in ethanol containing 50 g of ammonia were added to previously reduced platinum oxide (2.38 g of platinum oxide in 320 ml of alcohol and 10 ml of glacial acetic acid). Reduction was carried out at atmospheric pressure; it proceeded with evolution of heat. In the course of nine hours 35 liters of hydrogen was absorbed. The reaction mixture was diluted with water until the ammonium chloride was dissolved, and it was then filtered. The precipitate of 1,5,5,6,6,10-hexachlorodecane was dissolved in chloroform, and the solution was dried over calcium chloride. The solvent was removed, and low-boiling substances (180 g) were removed under reduced pressure. The hexachlorodecane, which remained behind, was recrystallized from alcohol. The product was 202 g (48.5%) of hexachlorodecane, m.p. 84-85°.

Fractionation of the low-boiling products through a column yielded 50 g of the original 1,1,1,5-tetrachloropentane and 105 g of 1,1,5-trichloropentane, b.p. 84° (8 mm);  $n_D^{20}$  1.4788;  $d_4^{20}$  1.2438; found MR 39.93; calculated MR 39.89.

Found %: C 34.30; 34.18; H 5.17; 5.30

$C_8H_2Cl_6$ . Calculated %: C 34.18; H 5.12

b) A mixture consisting of 100 g of 1,1,1,5-tetrachloropentane, a solution of 19 g of caustic soda in 50 ml of water, and 3 g of Raney nickel was shaken at 60-90° until hydrogen ceased to be absorbed (12 hours). The product was extracted with chloroform. The chloroform was removed, and the low-boiling part was distilled off under reduced pressure (54.7 g). The amount of 1,5,5,6,6,10-hexachlorodecane obtained was 21.1 g (25.4%).

c) Raney nickel (10 g) was added gradually to a solution of 21 g of tetrachloropentane in 50 ml of alcohol; much heat was evolved. The mixture was boiled for two hours, the catalyst was filtered off, and the oil present was extracted with chloroform. The low-boiling products were distilled off, and 3.5 g (20%) of 1,5,5,6,6,10-hexachlorodecane was obtained. It melted at 83-84°.

### Hydrogenation of 1,1,1,7-Tetrachloroheptane to 1,7,7,8,8,14-Hexachlorotetradecane

1,1,1,7-Tetrachloroheptane (83 g) and a solution of 8 g of ammonia in 80 ml of methanol were added to previously reduced 5% Pd/BaSO<sub>4</sub> (2 g) in 25 ml of methanol and 1 ml of glacial acetic acid. During the hydrogenation the reaction mixture became warm. After three hours, when 6.1 liters of hydrogen had been absorbed, the absorption of hydrogen ceased. The methanolic solution was filtered from the catalyst and ammonium chloride, and the precipitate was washed with chloroform on the filter. Water was added to the filtrate. The chloroform layer was dried over calcium chloride. After removal of chloroform under reduced pressure, the low-boiling products were distilled off (28 g). Recrystallization of the residue from ethanol yielded 32.1 g (45.5%) of 1,7,7,8,8,14-hexachlorotetradecane, m.p. 57-58°. Fractionation of the low-boiling products through a column yielded 16 g of 1,1,7-trichloroheptane, b.p. 74-75 (1.5 mm);  $n_D^{20}$  1.4776;  $d_4^{20}$  1.1744; found MR 49.13, calculated MR 49.13.

Found %: C 41.08; 41.12; H 6.19; 6.34

$C_7H_{13}Cl_3$ . Calculated %: C 41.24; H 6.38

### Hydrogenation of 1,1,1,5-Tetrachloropentane to 1,1,5-Trichloropentane

A mixture of 63 g of tetrachloropentane, 25 g of pyridine, and 80 ml of methanol was treated with hydrogen at 100 atm in presence of 5 g of Raney nickel at room temperature. The catalyst was filtered off, and the filtrate was diluted with water and extracted with chloroform. The extract was washed with dilute hydrochloric acid. After removal of chloroform, the residue was fractionated through a column and yielded 42 g (80%) of 1,1,5-trichloropentane.

### Hydrogenation of 1,1,1,5-Tetrachloropentane to 1,5,6,10-Tetrachloro-5-decene

Tetrachloropentane (63 g) was hydrogenated in presence of 0.2 g of PtO<sub>2</sub> and 5.5 g of ammonia in 80 ml of methanol for 2 hours 30 minutes, in the course of which 5.2 liters of hydrogen was absorbed. The mixture was then cooled, and 5.2 g of ammonia was passed in. In the course of further hydrogenation for two hours, a further 5.6 liters of hydrogen was absorbed. The usual treatment yielded 19.2 g (45.5%) of 1,5,6,10-tetrachloro-5-decene, b.p. 152-154° (3 mm);  $n_D^{20}$  1.5055;  $d_4^{20}$  1.2202; found MR 67.56; calculated MR 67.38.

Found %: C 43.37; 43.41; H 5.91; 6.21

$C_{10}H_{16}Cl_4$ . Calculated %: C 43.16; H 5.75

#### Action of Zinc on 1,5,5,6,6,10-Hexachlorodecane

A stirred mixture of 50 g of 1,5,5,6,6,10-hexachlorodecane, 20 g of zinc dust, and 150 ml of ethanol was boiled for six hours. Chloroform was added to the reaction mixture and the zinc was filtered off. Water and a little concentrated hydrochloric acid were added to the filtrate. The chloroform solution was dried over calcium chloride. Vacuum distillation yielded 37.2 g (95%) of 1,5,6,10-tetrachloro-5-decene.

#### Ozonization of 1,5,6,10-Tetrachloro-5-decene

A solution of 5 g of 1,5,6,10-tetrachloro-5-decene in 60 ml of dry chloroform was treated with 6% ozone for six hours. The reaction mixture was diluted with water, heated for a time at 50-60°, and then boiled for 5-6 hours. The mixture was extracted with chloroform. After removal of solvent, 1.5 g of 5-chlorovaleric acid was isolated and was identified in the form of its anilide, which showed no melting point depression in admixture with known 5-chlorovalerianilide.

#### Hydrogenation of 1,1,1,7-Tetrachloroheptane to 1,7,8,14-Tetrachloro-7-tetradecene

Tetrachloroheptane (90 g) was hydrogenated in presence of 1.5 g of Pd/BaSO<sub>4</sub> and 8.3 g of ammonia in 100 ml of methanol for three hours, in the course of which six liters of hydrogen was absorbed. The reaction mixture was cooled, and 8.1 g of ammonia was passed in. During further hydrogenation for three hours, a further 7.5 liters of hydrogen was absorbed. The usual treatment yielded 28 g (44%) of 1,7,8,14-tetrachloro-7-tetradecene, b.p. 178-180° (2 mm);  $n_D^{20}$  1.4980;  $d_4^{20}$  1.1393; found MR 85.94; calculated MR 85.85.

Found %: C 50.18; 50.07; H 7.40; 7.29

C<sub>14</sub>H<sub>2</sub>Cl<sub>4</sub>. Calculated %: C 50.29; H 7.20

#### Action of Zinc on 1,7,7,8,8,14-Hexachlorotetradecane

Hexachlorotetradecane (15 g) was added gradually to a stirred mixture of 5 g of zinc dust (previously activated by heating it with 0.1 ml of glacial acetic acid and 0.1 ml of hydrobromic acid) and 30 ml of absolute alcohol. Reaction proceeded with evolution of much heat. After the mixture had been heated for one hour and cooled, chloroform was added. The excess of zinc was filtered off, and dilute hydrochloric acid was added to the filtrate. The chloroform layer was separated, washed with water, and dried with calcium chloride. Vacuum distillation yielded 11.5 g (92%) of 1,7,8,14-tetrachloro-7-tetradecene.

#### Hydrogenation of 1,7,7,8,8,14-Hexachlorotetradecane to 1,7,8,14-Tetrachloro-7-tetradecene

Hexachlorotetradecane (20 g) was hydrogenated in presence of 1 g of Pd/BaSO<sub>4</sub> and 1.8 g of ammonia in 50 ml of methanol for two hours, in the course of which 1.2 liters of hydrogen was absorbed. The usual treatment yielded 13.6 g (81%) of tetrachlorotetradecene.

#### 1,10-Dichlorodecane

a) Tetrachlorodecane (15 g) was hydrogenated in presence of 1 g of Pd/BaSO<sub>4</sub> and 2.3 g of ammonia in 70 ml of methanol for five hours, in the course of which 3.6 liters of hydrogen was absorbed. Fractionation of the products yielded 7.6 g (67%) of 1,10-dichlorodecane, b.p. 105-106° (1.5 mm);  $n_D^{20}$  1.4620;  $d_4^{20}$  0.9992; found MR 58.05; calculated MR 58.11. The literature [8] gives b.p. 147-148° (11 mm);  $d_4^{20}$  0.9940.

b) A mixture of 100 g of 1,5,5,6,6,10-hexachlorodecane, 100 g of diethylamine, 200 ml of ethanol, and 12 g of Raney nickel was placed in a one-liter rotating autoclave. Hydrogen was passed into the autoclave until the pressure attained 100 atm. The reaction was carried out at 50-55°, hydrogen being passed in as necessary so that the pressure was maintained at 100-120 atm. After eight hours reaction ceased. The products obtained were 41 g (63%) of 1,10-dichlorodecane and 15 g (19%) of 1,5,6,10-tetrachlorodecane.

#### 1,14-Dichlorotetradecane

a) Tetrachlorotetradecene (28 g) was hydrogenated in presence of 2 g of Pd/BaSO<sub>4</sub> and 13 g of diethylamine in 70 ml of methanol for five hours, in the course of which 3.7 liters of hydrogen was absorbed. Dichlorotetradecane is of low solubility in methanol and was to be found mainly in the precipitate. The product was 15.1 g (67%) of 1,14-dichlorotetradecane, b.p. 143-144° (1.5 mm); m.p. 38-39° (from methanol).

Found %: C 63.06; 63.13; H 10.20; 10.44

C<sub>14</sub>H<sub>22</sub>Cl<sub>2</sub>. Calculated %: C 62.92; H 10.48

Reduction was slower in presence of ammonia.

b) Tetrachloroheptane (90 g) was hydrogenated in presence of 1.5 g of Pd/BaSO<sub>4</sub> and 8.1 g of ammonia in 100 ml of methanol for 2 hours 30 minutes, in the course of which 7.5 liters of hydrogen was absorbed. The catalyst and ammonium chloride were filtered off, methanol was distilled off, and low-boiling fractions were removed under reduced pressure. The residue (42 g) was hydrogenated in presence of 3 g of Pd/BaSO<sub>4</sub> and 32 g of diethylamine in 80 ml of ethanol for ten hours. The product was 14.5 g (28%) of 1,14-dichlorotetradecane, b.p. 144-146° (1.5 mm), together with about 5 g of a mixture boiling at 150-180° (1 mm) and consisting mainly of tetrachlorotetradecene.

#### Hydrogenation of 1.1.1 2.5-Pentachloropentane

Pentachloropentane (20 g) and 39 ml of a solution of ammonia in ethanol containing 19.5 g of ammonia were added to previously reduced platinum oxide (0.18 g of PtO<sub>2</sub> in 15.0 ml of ethanol and 0.8 ml of glacial acetic acid). The mixture was shaken with hydrogen for two hours, in the course of which 4 liters of hydrogen was absorbed. The usual treatment and vacuum distillation yielded 4.5 g of the original compound and 8 g (74%) of 1.1.5-trichloro-1-pentene, b.p. 72-74° (10 mm);  $n_D^{20}$  1.4902;  $d_4^{20}$  1.2734. The literature [9] gives b.p. 68-69° (7 mm);  $n_D^{20}$  1.4892;  $d_4^{20}$  1.2724.

#### 6.7-Dichloro-6-dodecenedinitrile

A stirred mixture of 20 g of tetrachlorododecene, 11 g of sodium cyanide, 1 g of sodium iodide, 5 ml of water and 40 ml of 2-ethoxyethanol was heated at 102-106° for four hours. The mixture was cooled, diluted with water, and extracted with chloroform. Vacuum distillation yielded 16.5 g (88%) of 6,7-dichloro-6-dodecenedinitrile, b.p. 212-214° (45 mm);  $n_D^{20}$  1.4943;  $d_4^{20}$  1.1295; found, MR 66.80; calculated, MR 66.52.

Found %: N 10.77; 10.73  
C<sub>12</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>.      Calculated %: N 10.81.

#### 8.9-Dichloro-8-hexadecenedinitrile

A stirred mixture of 32 g of tetrachlorotetradecene, 12 g of sodium cyanide, 0.5 g of sodium iodide, 5 ml of water, and 60 ml of 2-ethoxyethanol was heated at 102-106° for six hours. The mixture was cooled, diluted with water, and extracted with chloroform. Vacuum distillation yielded 26 g (80%) of 8,9-dichloro-8-hexadecenedinitrile, b.p. 212-213°;  $n_D^{20}$  1.4895;  $d_4^{20}$  1.0704; found MR 85.01; calculated MR 85.00.

Found %: N 8.56; 8.58  
C<sub>16</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>2</sub>.      Calculated %: N 8.89

#### 6.7-Dichloro-6-dodecenedioic Acid

A solution containing 14.5 g of 6,7-dichloro-6-dodecenedinitrile, 60 ml of glacial acetic acid, 35 ml of concentrated hydrochloric acid, and 18 ml of water was boiled for 15 hours. Addition of water and cooling yielded a precipitate of the acid, amounting to 15.3 g (92%); m.p. 108.5-109.5° (from benzene).

Found %: C 48.66, 48.86; H 6.16, 6.18  
C<sub>12</sub>H<sub>18</sub>Cl<sub>2</sub>O<sub>4</sub>.      Calculated %: C 48.48;      H 6.06

#### 8.9-Dichloro-8-hexadecenedioic Acid

Dichlorohexadecenedinitrile (6.5 g) was hydrolyzed by heating it with a mixture of 30 ml of glacial acetic acid, 15 ml of concentrated hydrochloric acid, and 8 ml of water for 20 hours. The yield of acid was 6.8 g (94%), m.p. 95-96° (from benzene).

Found %: C 54.52, 54.58; H 7.10, 7.24  
C<sub>16</sub>H<sub>26</sub>Cl<sub>2</sub>O<sub>4</sub>.      Calculated %: C 54.39;      H 7.36

#### Dodecanedioic Acid

Dichlorododecenedioic acid (10.2 g) was dissolved in aqueous alkali (8 g of caustic soda in 80 ml of water) and hydrogenated in presence of 3 g of nickel catalyst at 60-70° and 100 atm for two hours. The catalyst was filtered off, and the filtrate was acidified with hydrochloric acid, when 7.3 g (92%) of dodecanedioic acid was obtained. Hexadecanedioic acid was prepared similarly from dichlorohexadecenedioic acid in 93% yield.



### Hexadecanedinitrile

Dichlorododecenedinitrile (12 g) was hydrogenated in presence of 1.5 g of Pd/BaSO<sub>4</sub> and 10 g of diethylamine in 60 ml of methanol for 90 minutes, in the course of which 2.7 liters of hydrogen was absorbed. The catalyst was filtered off, and the filtrate was diluted with water, acidified with hydrochloric acid, and extracted with benzene. The residue remaining after removal of benzene crystallized out, and 9.1 g of hexadecanedinitrile, m.p. 48-49° (from a mixture of petroleum ether and benzene), was obtained.

Found %: N 11.12, 11.18  
C<sub>16</sub>H<sub>28</sub>N<sub>2</sub> Calculated %: N 11.29

### 6,6,7,7-Tetrachlorododecanedioic Acid

A stirred mixture of 20 g of 1,5,5,6,6,10-hexachlorodecane, 150 ml of 2-ethoxyethanol, and 5 g of sodium cyanide was heated at 110° for five hours. The mixture was cooled, and the precipitate present was filtered off and washed with water. The yield of crude tetrachlorododecenedinitrile was 12.2 g. A mixture of 10 g of the dinitrile, 20 ml of glacial acetic acid, and 40 ml of hydrochloric acid (1:1) was boiled for 12 hours. The precipitate that formed was filtered off and treated with hot alkali. Treatment of the sodium salt with hydrochloric acid yielded 9 g (80.8%) of 6,6,7,7-tetrachlorododecanedioic acid, m.p. 223° (from ethanol).

Found %: C 39.71, 39.52; H 4.97, 4.97; Cl 38.46; 38.67  
C<sub>10</sub>H<sub>10</sub>O<sub>4</sub>Cl<sub>4</sub> Calculated %: C 39.13; H 4.92; Cl 38.58

### Dodecanedinitrile

A stirred mixture of 11 g of 1,10-dichlorodecane, 7.5 g of sodium cyanide, 0.5 g of sodium iodide, 5 ml of water, and 25 ml of 2-ethoxyethanol was heated for four hours. The product was 9.3 g (92%) of dodecanedinitrile, b.p. 156-157° (2 mm). In a similar way, hexadecanedinitrile was prepared from 1,14-dichlorotetradecane in a 90% yield.

### SUMMARY

1. Dodecanedioic and hexadecanedioic acids were synthesized from 1,1,1,5-tetrachloropentane and 1,1,1,7-tetrachloroheptane respectively.
2. The reductive dimerization of 1,1,1,5-tetrachloropentane and 1,1,1,7-tetrachloroheptane was investigated. It was found that platinum and palladium catalysts give better results than Raney nickel under the conditions studied.
3. It was shown that the reduction of  $\alpha,\alpha,\alpha,\omega$ -tetrachloroalkanes to dimeric  $\alpha,\omega$ -dichloroalkanes passes through the stage of unsaturated tetrachloro compounds containing the  $-\text{CCl}=\text{CCl}$  grouping, which is more readily reduced than the  $\text{CH}_2\text{Cl}$  group.

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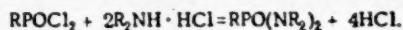
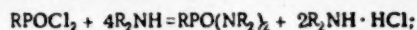


# DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

## COMMUNICATION 8. BISDIALKYLAMIDES OF 2-ALKOXY- AND 2-PHENOXY-VINYLPHOSPHONIC ACIDS

K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov

Amides of alkyl- and aryl-phosphonic acids have been prepared by numerous investigators [1-7] by the reaction of alkyl- and aryl-phosphonic dichlorides with amines or their hydrochlorides:



There are no data relating to amides of unsaturated phosphonic acids in the scientific literature, but there is an isolated reference to the compound  $\text{CH}_2=\text{C}(\text{CH}_3)\text{PO}[\text{N}(\text{CH}_3)_2]_2$  in the patent literature [8]. As we could readily prepare 2-alkoxy- and 2-phenoxy-vinylphosphonic dichlorides by the method that we have developed [9], we synthesized some bisdialkylamides of 2-alkoxy- and 2-phenoxy-vinylphosphonic acids by reaction between one molecule of the acid chloride and four molecules of the secondary amine in an inert solvent.

The bisdialkylamides of 2-alkoxy- and 2-phenoxy-vinylphosphonic acids are viscous liquids that are readily distilled under reduced pressure and are stable to storage. They were obtained in yields of up to 80%. The formulas of the compounds prepared are given with their physical properties in the table.

TABLE

Formula	B.p. in °C (p in mm)	$n_D^{20}$	$d_4^{20}$
$\text{C}_2\text{H}_5\text{-O-CH=CHPO}[\text{N}(\text{CH}_3)_2]_2$	108 (1)	1.4780	1.0401
$i\text{-C}_3\text{H}_7\text{-O-CH=CHPO}[\text{N}(\text{CH}_3)_2]_2$	105.5 (2)	1.4742	1.0182
$n\text{-C}_4\text{H}_9\text{-O-CH=CHPO}[\text{N}(\text{CH}_3)_2]_2$	116 (1)	1.4755	1.0090
$\text{C}_6\text{H}_5\text{-O-CH=CHPO}[\text{N}(\text{CH}_3)_2]_2$	145 (2)	1.4858	1.1199
$\text{C}_2\text{H}_5\text{-O-CH=CHPO}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	126.5 (2)	1.4755	1.0950
$i\text{-C}_3\text{H}_7\text{-O-CH=CHPO}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	132 (2)	1.4709	0.9962
$n\text{-C}_4\text{H}_9\text{-O-CH=CHPO}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	130 (2)	1.4729	0.9745
$\text{C}_6\text{H}_5\text{-O-CH=CHPO}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	161 (2)	1.5200	1.0402
$\text{C}_2\text{H}_5\text{-O-CH=CHPO}[\text{N}(\text{C}_4\text{H}_9\text{-}n)_2]_2$	172 (2)	1.4680	0.9399
$n\text{-C}_3\text{H}_7\text{-O-CH=CHPO}[\text{N}(\text{C}_4\text{H}_9\text{-}n)_2]_2$	172 (2)	1.4678	0.9301
$(\text{CH}_3)_2\text{-CH-CH}_2\text{-CH}_2\text{-O-CH=CHPO}[\text{N}(\text{C}_4\text{H}_9\text{-}n)_2]_2$	192-193 (2)	1.4691	0.9249
$\text{C}_6\text{H}_5\text{-O-CH=CHPO}[\text{N}(\text{C}_4\text{H}_9\text{-}n)_2]_2$	212 (0.5)	1.5060	0.9886
$\text{C}_2\text{H}_5\text{-O-CH=CHPO}[\text{N}(\text{C}_5\text{H}_{11})_2]_2$	m.p. 60-61		
$\text{C}_6\text{H}_5\text{-O-CH=CHPO}[\text{N}(\text{C}_5\text{H}_{11})_2]_2$	202 (1)	1.5528	1.1193

## EXPERIMENTAL

Bisdimethylamide of 2-ethoxyvinylphosphonic acid  $\text{C}_2\text{H}_5\text{-O-CH=CHPO}[\text{N}(\text{CH}_3)_2]_2$ . 2-Ethoxyvinylphosphonic dichloride (9.45 g) was added to a well-cooled, stirred mixture of 100 ml of petroleum ether and 9 g of dimethylamine contained in a three-necked flask fitted with stirrer, reflux condenser and dropping funnel. When the whole of the acid chloride had been added, stirring was continued for two hours. The mixture was set aside overnight and then heated at 55-60° in a water bath for two hours. The precipitate of dimethylamine hydrochloride was filtered off and washed three times with petroleum ether. The filtrate was then treated with a saturated solution of caustic soda and dried over calcined potassium carbonate. Petroleum ether and benzene

were distilled off, and the residue was left in the boiling water bath for 30 minutes and then vacuum-distilled. Three fractionations yielded 6.4 g (57%) of a substance of b.p. 108° (1 mm);  $n_D^{20}$  1.4780;  $d_4^{20}$  1.0401.

Found %: N 13.54, 13.26

$C_8H_{13}O_2PN_2$ . Calculated %: N 13.59

Bisdiethylamide of 2-ethoxyvinylphosphonic acid  $C_2H_5-O-CH=CHPO[N(C_2H_5)_2]_2$ . 2-Ethoxyvinylphosphonic dichloride (10 g) was added from a dropping funnel to a cooled, stirred mixture of 100 ml of petroleum ether and 17 g of diethylamine. The reaction mixture was then treated as described above, and three fractionations yielded 8 g (59%) of a substance of b.p. 126.5° (1.5 mm);  $n_D^{20}$  1.4755;  $d_4^{20}$  0.0950.

Found %: N 10.37, 10.26

$C_{12}H_{27}O_2PN_2$ . Calculated %: N 10.68

Bisdibutylamide of 2-ethoxyvinylphosphonic acid  $C_2H_5-O-CH=CHPO[N(C_4H_9)_2]_2$ . 2-Ethoxyvinylphosphonic dichloride (9.5 g) was added to a mixture of 28 g of dibutylamine and 130 ml of petroleum ether. Fractionation yielded 12 g of the bisdibutylamide of 2-ethoxyvinylphosphonic acid, b.p. 172° (2 mm);  $n_D^{20}$  1.4660;  $d_4^{20}$  0.9399.

Found %: P 8.13, 8.26

$C_{26}H_{48}PO_2N_2$ . Calculated %: P 8.26

Dipiperidide of 2-ethoxyvinylphosphonic acid  $C_2H_5OCH=CHPO[NC_5H_{10}]_2$ . From 18 g of piperidine and 9.45 g of 2-ethoxyvinylphosphonic dichloride, 13.8 g of the dipiperidide of 2-ethoxyvinylphosphonic acid was obtained. After recrystallization from a mixture of petroleum ether and benzene it melted at 60-61°.

Found %: P 10.78, 10.82

$C_{14}H_{27}PO_2N_2$ . Calculated %: P 10.83

Bisdibutylamide of 2-propoxyvinylphosphonic acid  $n-C_3H_7OCH=CHPO[N(C_4H_9)_2]_2$ . 2-Propoxyvinylphosphonic dichloride (10.2 g) was added to a solution of 28 g of dibutylamine in 150 ml of petroleum ether. The product isolated (13 g) had b.p. 172° (1 mm);  $n_D^{20}$  1.4663;  $d_4^{20}$  0.9301.

Found %: N 7.64, 7.48

$C_{21}H_{45}O_2PN_2$ . Calculated %: N 7.21

Bisdimethylamide of 2-isopropoxyvinylphosphonic acid  $i-C_3H_7-O-CH=CHPO[N(CH_3)_2]_2$ . A solution of 9 g of dimethylamine in 10 ml of petroleum ether was added to a cooled mixture of 50 ml of petroleum ether and 50 ml of benzene, and then 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added. The substance isolated (8 g, i.e., 73%) had b.p. 105.5° (2 mm);  $n_D^{20}$  1.4742;  $d_4^{20}$  1.0182.

Found %: N 12.55, 12.68

$C_{10}H_{21}PO_2N_2$ . Calculated %: N 12.72

Bisdiethylamide of 2-isopropoxyvinylphosphonic acid  $i-C_3H_7-O-CH=CHPO[N(C_2H_5)_2]_2$ . Reaction between 14.5 g of diethylamine and 10.15 g of 2-isopropoxyvinylphosphonic dichloride yielded 7.5 g (55%) of a substance having b.p. 132° (2 mm);  $n_D^{20}$  1.4709;  $d_4^{20}$  0.9952.

Found %: N 10.07, 9.92

$C_{13}H_{29}O_2PN_2$ . Calculated %: N 10.14

Bisdimethylamide of 2-butoxyvinylphosphonic acid  $n-C_4H_9-O-CH=CHPO[N(CH_3)_2]_2$ . Reaction between 10.85 g of 2-butoxyvinylphosphonic dichloride and 9 g of dimethylamine in a mixture of 50 ml of petroleum ether and 50 ml of benzene as solvent yielded 6 g (50%) of a substance having b.p. 116° (1 mm);  $n_D^{20}$  1.4755;  $d_4^{20}$  1.0090.

Found %: P 13.26, 13.20

$C_{10}H_{23}O_2N_2P$ . Calculated %: P 13.24

Bisdiethylamide of 2-butoxyvinylphosphonic acid  $n-C_4H_9-O-CH=CHPO[N(C_2H_5)_2]_2$ . 2-Butoxyvinylphosphonic dichloride (10.85 g) was added gradually to 14.5 g of diethylamine. Three fractionations yielded 8 g (55%) of a substance having b.p. 130° (1 mm);  $n_D^{20}$  1.4729;  $d_4^{20}$  0.9745.

Found %: N 9.66, 9.29

$C_{14}H_{31}O_2N_2P$ . Calculated %: N 9.65

Bisdibutylamide of 2-isopentyloxyvinylphosphonic acid  $(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO[N(C_4H_9)_2]_2$ . To 28 g of dibutylamine, 11.55 g of 2-isopentyloxyvinylphosphonic dichloride was added. The product isolated (10.3 g) had b.p. 192-193° (2 mm);  $n_D^{20}$  1.4665;  $d_4^{20}$  0.9249.

Found %: N 6.87, 6.91

$C_{23}H_{49}PO_2N_2$ . Calculated %: N 6.73

Bisdimethylamide of 2-phenoxyvinylphosphonic acid  $C_6H_5-O-CH=CHPO[N(CH_3)_2]_2$ . To 9.5 g of dimethylamine, 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. The yield of product was 6.5 g (50%), and it had b.p. 145° (2 mm);  $n_D^{20}$  1.4658;  $d_4^{20}$  1.1199.

Found %: N 10.90, 11.06

$C_{12}H_{15}O_2PN_2$ . Calculated %: N 11.02

Bisdiethylamide of 2-phenoxyvinylphosphonic acid  $C_6H_5-O-CH=CHPO[N(C_2H_5)_2]_2$ . Reaction between 14.5 g of diethylamine and 11.85 g of 2-phenoxyvinylphosphonic dichloride yielded 9 g (58%) of a substance having b.p. 132° (1 mm);  $d_4^{20}$  1.0402;  $n_D^{20}$  1.5200.

Found %: N 8.94, 8.98

$C_{16}H_{21}O_2PN_2$ . Calculated %: N 9.03

Bisdibutylamide of 2-phenoxyvinylphosphonic acid  $C_6H_5OCH=CHPO[N(C_4H_9)_2]_2$ . The bisdibutylamide of 2-phenoxyvinylphosphonic acid (12.5 g) was prepared from 27 g of dibutylamine and 11.85 g of 2-phenoxyvinylphosphonic dichloride. It had b.p. 213° (0.5 mm);  $n_D^{20}$  1.5060;  $d_4^{20}$  0.9886.

Found %: P 7.39, 7.24

$C_{24}H_{43}PO_2N_2$ . Calculated %: P 7.34

Dipiperidide of 2-phenoxyvinylphosphonic acid  $C_6H_5OCH=CHPO(NC_4H_9)_2$ . To 16.52 g of piperidine, 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. Suitable treatment yielded 10 g of the dipiperidide of 2-phenoxyvinylphosphonic acid, b.p. 202° (1 mm);  $n_D^{20}$  1.5528;  $d_4^{20}$  1.1193.

Found %: P 9.29, 9.23

$C_{18}H_{27}PO_2N_2$ . Calculated %: P 9.28

#### SUMMARY

The following compounds were synthesized by the reaction of secondary aliphatic amines with 2-alkoxy- and 2-phenoxyvinylphosphonic dichlorides: the bisdimethylamides of 2-ethoxy-, 2-isopropoxy-, 2-butoxy-, and 2-phenoxyvinylphosphonic acids; the bisdiethylamides of 2-ethoxy-, 2-isopropoxy-, 2-butoxy-, and 2-phenoxyvinylphosphonic acids; the bisdibutylamides of 2-ethoxy-, 2-propoxy-, 2-isopentyloxy-, and 2-phenoxyvinylphosphonic acids; and the dipiperidides of 2-ethoxy-, 2-butoxy-, and 2-phenoxyvinylphosphonic acids.

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\* T.p. = Consultants Bureau Translation pagination.

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# DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

## COMMUNICATION 9. DIESTERS OF 2-ALKOXY- AND 2-PHENOXY-VINYLPHOSPHONOTHIONIC ACIDS

K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov

As shown in previous communications [1, 2], 2-alkoxy- and 2-phenoxy-vinylphosphonic dichlorides react fairly readily with alcohols and with secondary amines, forming diesters and bisdialkylamides, respectively, of 2-alkoxy- and 2-phenoxy-vinylphosphonic acids. 2-Alkoxy- and 2-phenoxy-vinylphosphonothionic dichlorides are considerably more inert, and they do not react with alcohols or with amines under the conditions that we have described previously for the synthesis of esters and bisdialkylamides of unsaturated phosphonic acids.

We have now prepared diesters of 2-alkoxy- and 2-phenoxy-vinylphosphonothionic acids by the action of the corresponding acid chlorides on a sodium alkoxide in an excess of the alcohol. The compounds listed in the table were synthesized under these conditions. The 2-alkoxy- and 2-phenoxy-vinylphosphonothionic dichlorides were prepared by a method developed by us [3]. All of the esters that we have prepared are colorless liquids, which are insoluble in water, but soluble in ether, benzene, acetone, and other organic solvents.

TABLE

Formula	B.p. in °C (p in mm)	$n_D^{20}$	$d_4^{20}$
$C_2H_5-O-CH=CHPS(OCH_3)_2$ . . . . .	86 (1)	1.4852	1.1373
$i-C_3H_7-O-CH=CHPS(OCH_3)_2$ . . . . .	95 (1)	1.4780	1.1035
$n-C_4H_9-O-CH=CHPS(OCH_3)_2$ . . . . .	107 (1)	1.4790	1.1018
$C_6H_5-O-CH=CHPS(OCH_3)_2$ . . . . .	151 (2)	1.5331	1.1945
$C_2H_5-O-CH=CHPS(OC_2H_5)_2$ . . . . .	107 (3)	1.4879	1.0970
$i-C_3H_7-O-CH=CHPS(OC_2H_5)_2$ . . . . .	105 (1)	1.4741	1.0510
$n-C_4H_9-O-CH=CHPS(OC_2H_5)_2$ . . . . .	117 (1)	1.4705	1.0687
$C_6H_5-O-CH=CHPS(OC_2H_5)_2$ . . . . .	159 (2)	1.5375	1.1263

### EXPERIMENTAL

Dimethyl 2-ethoxyvinylphosphonothionate  $C_2H_5-O-CH=CHPS(OCH_3)_2$ . Absolute methanol (50 ml) and sodium (2.3 g) were introduced into a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. The resulting solution of sodium methoxide was cooled, and was then stirred while 10.2 g of 2-ethoxyvinylphosphonothionic dichloride was added gradually. When the whole of this had been added, the mixture was stirred for three hours and was then set aside overnight. On the next day 100 ml of absolute ether was added to the mixture. The mixture was warmed in a water bath (55-60°), where it was stirred for two hours. The ether layer was poured off and the precipitate was washed twice with ether. The ether solution was dried over  $Na_2SO_4$ . Vacuum fractionation yielded 6.5 g (60%) of a substance having b.p. 86° (1 mm);  $n_D^{20}$  1.4852;  $d_4^{20}$  1.1373.

Found %: P 15.81, 15.72

$C_6H_{13}O_3PS$ . Calculated %: P 15.81

Dimethyl 2-isopropoxyvinylphosphonothionate  $i-C_3H_7-O-CH=CHPS(OCH_3)_2$ . 2-Isopropoxyvinylphosphonothionic dichloride (10.95 g) was diluted with an equal volume of absolute methanol and then added with cooling and stirring to a solution of sodium methoxide prepared from 50 ml of absolute methanol and 2.3 g of sodium. The product isolated (9.7 g, i.e., 86%) had b.p. 101° (2 mm);  $n_D^{20}$  1.4780;  $d_4^{20}$  1.1035.

Found %: P 14.73, 14.69

$C_7H_{15}O_3PS$ . Calculated %: P 14.76

Dimethyl 2-butoxyvinylphosphonothionate  $n\text{-C}_4\text{H}_9\text{-O-CH=CHPS(OCH}_3)_2$ . A solution of 11.65 g of 2-butoxyvinylphosphonothionic dichloride in 12 ml of absolute methanol was added to sodium methoxide prepared from 2.3 g of sodium and 56 ml of absolute methanol. The pure product isolated (9.1 g, i.e., 70%) had b.p.  $107^\circ$  (1 mm);  $n_D^{20}$  1.4790;  $d_4^{20}$  1.1018.

Found %: P 13.88, 13.81

$\text{C}_8\text{H}_{17}\text{O}_3\text{PS}$ . Calculated %: P 13.83

Dimethyl 2-phenoxyvinylphosphonothionate  $\text{C}_6\text{H}_5\text{-O-CH=CHPS(OCH}_3)_2$ . A solution of 12.65 g of 2-phenoxyvinylphosphonothionic dichloride in 20 ml of absolute methanol was added to sodium methoxide prepared from 50 ml of absolute methanol and 2.3 g of sodium. Vacuum fractionation of the crude product (9 g) yielded 6.6 g (50%) of a substance having b.p.  $151^\circ$  (2 mm);  $n_D^{20}$  1.5531;  $d_4^{20}$  1.1945.

Found %: P 12.59, 12.60

$\text{C}_{10}\text{H}_{13}\text{O}_3\text{PS}$ . Calculated %: P 12.70

Diethyl 2-ethoxyvinylphosphonothionate  $\text{C}_2\text{H}_5\text{-O-CH=CHPS(OC}_2\text{H}_5)_2$ . 2-Ethoxyvinylphosphonothionic dichloride (12.2 g) was added to sodium ethoxide prepared from 2.3 g of sodium and 60 ml of absolute ethanol. The product isolated (6.2 g, i.e., 50%) had b.p.  $100^\circ$  (1 mm);  $n_D^{20}$  1.4879;  $d_4^{20}$  1.0970.

Found %: P 13.87, 13.64

$\text{C}_8\text{H}_{17}\text{O}_3\text{PS}$ . Calculated %: P 13.83

Diethyl 2-isopropoxyvinylphosphonothionate  $i\text{-C}_3\text{H}_7\text{-O-CH=CHPS(OC}_2\text{H}_5)_2$ . 2-Isopropoxyvinylphosphonothionic dichloride (10.95 g) was added to sodium ethoxide prepared from 50 ml of absolute ethanol and 2.3 g of sodium. The product isolated (8 g, i.e., 63%) had b.p.  $105^\circ$  (1 mm);  $n_D^{20}$  1.4741;  $d_4^{20}$  1.0510.

Found %: P 13.07, 12.89

$\text{C}_9\text{H}_{19}\text{O}_3\text{PS}$ . Calculated %: P 13.02

Diethyl 2-butoxyvinylphosphonothionate  $n\text{-C}_4\text{H}_9\text{-O-CH=CHPS(OC}_2\text{H}_5)_2$ . 2-Butoxyvinylphosphonothionic dichloride (11.65 g) was added to sodium ethoxide prepared from 2.3 g of sodium and 80 ml of absolute ethanol. The product isolated (8 g, i.e., 60%) had b.p.  $107^\circ$  (1 mm);  $n_D^{20}$  1.4705;  $d_4^{20}$  1.0687.

Found %: P 12.27, 12.29

$\text{C}_{10}\text{H}_{21}\text{O}_3\text{PS}$ . Calculated %: P 12.30

Diethyl 2-phenoxyvinylphosphonothionate  $\text{C}_6\text{H}_5\text{-O-CH=CHPS(OC}_2\text{H}_5)_2$ . 2-Phenoxyvinylphosphonothionic dichloride (12.65 g) was added to sodium ethoxide prepared from 2.3 g of sodium and 50 ml of absolute ethanol. Fractionation of the crude product (12 g) yielded 7.8 g (75%) of a substance having b.p.  $139^\circ$  (2 mm);  $n_D^{20}$  1.5375,  $d_4^{20}$  1.1263.

Found %: P 11.43, 11.44

$\text{C}_{12}\text{H}_{15}\text{O}_3\text{PS}$ . Calculated %: P 11.39

#### SUMMARY

By the action of 2-ethoxy-, 2-isopropoxy-, 2-butoxy-, and 2-phenoxy-vinylphosphonothionic dichlorides on sodium methoxide and on sodium ethoxide in the form of solutions in the corresponding alcohols, the dimethyl and diethyl esters of 2-ethoxy-, 2-isopropoxy-, 2-butoxy-, and 2-phenoxy-vinylphosphonothionic acids were prepared.

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\* T.p. = Consultants Bureau Translation pagination.

## SOME ESTERS OF PHOSPHORODITHIOIC ACID AS INSECTICIDES

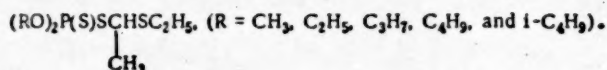
B. A. Arbuzov, K. V. Nikonov, and G. M. Vinokurova

As is well known, derivatives of thiophosphoric acids are used extensively in agriculture as insecticides; they are found to be very effective against many kinds of harmful insects. Among the many compounds of this sort there are the well known trimethyl phosphorothioate O,O-diethyl O-p-nitrophenyl phosphorothioate (parathion, thiophos), and the O-ester of 4-methylumbelliferone with O,O-diethyl phosphorothioate (potasan) [1]. O,O-Diethyl O-2-(ethylthio)ethyl phosphorothioate (systox) [2] is of great interest. This compound, while having a comparatively feeble contact action, is a good insecticide on account of internal (systemic) action. Systox can be used successfully as a nematocide [3].

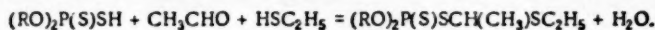
Interest has grown recently in the mixed esters of phosphorodithioic acid. These substances, while having fairly high insecticidal activity, are safer for warm-blooded animals, including man, than the esters of phosphoric and phosphorothioic acids [4]. A compound of this type that has found practical application in agriculture is S-[1,2-bis(ethoxycarbonyl)ethyl] O,O-dimethyl phosphorodithioate (malathion) [5].

In 1952 and 1953 some phosphorodithioic esters were described of general formula  $(RO)_2P(S)SCH(R')XR''$  ( $X = O$  or  $S$  and  $R, R',$  and  $R''$  are aliphatic or aromatic radicals). All of these were found to be powerful insecticides [6].

In this paper we describe the synthesis of compounds of the type



It was found that these substances can be readily prepared by the condensation of the corresponding O,O-dialkyl S-hydrogen phosphorodithioates with acetaldehyde and ethanethiol in accordance with the equation:



The resulting compounds were colorless liquids of unpleasant odor. The lower esters (up to propyl, inclusive) could be vacuum-distilled (at 2-3 mm) with partial decomposition; the butyl esters decomposed completely during distillation. The principal constants of the compounds obtained are given in Table 1.

The insecticidal activity of the compounds was tested on the corn weevil. The results of the tests are given in Table 2.

As can be seen from Table 2, the first two compounds have higher insecticidal activity than the succeeding compounds. On the whole, however, these esters are fairly weak insecticides. The tests for insecticidal activity were carried out in the toxicological laboratory of the Kazan Affiliated Institute of the Academy of Sciences of the USSR by M. A. Kudrina.

### EXPERIMENTAL

#### Action of Acetaldehyde and Ethanethiol on O,O-Dimethyl Phosphorodithioate

A mixture of 20 g of O,O-dimethyl phosphorodithioate and 8.1 g of ethanethiol was placed in a three-necked flask fitted with reflux condenser, thermometer, stirrer, and dropping funnel. The mixture was cooled to  $-10^\circ$  and stirred continuously while 5.5 g of acetaldehyde was added dropwise at such a rate that the temperature did not rise above  $0^\circ$ . When the addition was complete, stirring was continued for a further two hours at room temperature. After the whole of the aldehyde had been added the formation of some water (about 2 ml) was observed. This water was removed, and the organic layer was vacuum-distilled. Pure  $(CH_3O)_2P(S)SCH(CH_3)SC_2H_5$  has b.p.  $82-83^\circ$  (4 mm),  $n_D^{20} 1.5320$ ;  $n_D^{25} 1.51788$ . The yield was 28.70%.

Found %: P 12.95; 12.60

$C_6H_{15}S_2O_2P$ . Calculated %: P 12.6

TABLE 1

Formula	B.p. in °C (p in mm)	$d_4^{20}$	$n_D^{20}$	Yield (%)
$(CH_3O)_2PSCH(CH_3)SC_2H_5$    S	82-83 (4)	1.1788	1.5320	28.7
$(C_2H_5O)_2PSCH(CH_3)SC_2H_5$    S	118-119 (3)	1.1347	1.5240	39.6
Ditto (crude)	—	1.1351	1.5230	70.9
$(C_3H_7O)_2PSCH(CH_3)SC_2H_5$    S	122-128 (4)	1.0929	1.5130	49.3
$(C_4H_9O)_2PSCH(CH_3)SC_2H_5$ (crude)    S	—	1.0600	1.5085	73.5
$(i-C_4H_9O)_2PSCHSC_2H_5$ (crude)    S CH <sub>3</sub>	—	1.0522	1.5060	67.6

TABLE 2

Formula	Concentration (%)	Proportion of corn weevils killed (%)
$(CH_3O)_2PSCH(CH_3)SC_2H_5$    S	0.1 0.5 1	25 after 7 days 65 ditto 85 "
$(C_2H_5O)_2PSCH(CH_3)SC_2H_5$ (crude)    S	0.1 0.5 1	32 " 100 after 3 days 100 after 2 days
$(C_3H_7O)_2PSCH(CH_3)SC_2H_5$    S	0.1 0.5 1	12 after 7 days 16 ditto 18 "
$(C_4H_9O)_2PSCH(CH_3)SC_2H_5$ (crude)    S	0.1 0.5 1	12 " 20 " 24 "
$(i-C_4H_9O)_2PSCH(CH_3)SC_2H_5$ (crude)    S	0.1 0.5 1	6 " 10 " 12 "

#### Action of Acetaldehyde and Ethanethiol on O,O-Diethyl Phosphorodithioate

**Experiment 1.** Acetaldehyde (3.5 g) was added to a mixture of 15 g of O,O-diethyl phosphorodithioate and 5.01 g of ethanethiol. The water that separated was taken up with phosphoric oxide. The reaction mixture was stirred at room temperature for 30 minutes and then vacuum-distilled from an Arbuzov flask. The product isolated had b.p. 118-119° (3 mm);  $n_D^{20}$  1.5240;  $d_4^{20}$  1.1347. The yield was 39.6%

Found %: 12.18; 11.78; S 35.24

$C_8H_{19}O_2S_3P$ . Calculated %: P 11.31; S 35.04

**Experiment 2.** Reaction was between 20 g of O,O-diethyl phosphorodithioate, 4.7 g of acetaldehyde, and 6.6 g of ethanethiol. The reaction product was washed with 10% sodium carbonate solution and then water. It was then dried with calcium chloride and analyzed. The product had  $n_D^{20}$  1.5230 and  $d_4^{20}$  1.1351.

Found %: P 11.26; 11.19; S 35.22; 35.01

$C_8H_{19}O_2S_3P$ . Calculated %: P 11.31; S 35.06

#### Action of Acetaldehyde and Ethanethiol on O,O-Dipropyl Phosphorodithioate

The reactants were  $(C_3H_7O)_2PSSH$  (20 g),  $C_2H_5SH$  (5.9 g), and  $CH_3CHO$  (4.1 g). The reaction mixture was stirred at room temperature for four hours. Fractionation yielded two fractions: the first was unchanged dipropyl phosphorodithioate, and the second was the required ester, b.p. 122-128 (4 mm);  $n_D^{20}$  1.5130;  $d_4^{20}$  1.0929. The yield was 43%.



Found %: P 10.99, 10.92  
 $C_{10}H_{23}O_2PS_3$ . Calculated %: P 10.26

Action of Acetaldehyde and Ethanethiol on O,O-Dibutyl Phosphorodithioate

The procedure was as in the preceding experiment, the reactants being O,O-dibutyl phosphorodithioate (10 g), ethanethiol (2.5 g), and acetaldehyde (1.8 g). The reaction product was washed with 10% aqueous sodium carbonate solution and with water, then dried with calcium chloride and analyzed. The product had  $n_D^{20}$  1.5085;  $d_4^{20}$  1.060. The yield was 73.5%.

Found %: P 9.46; 9.35  
 $C_{12}H_{27}S_3PO_2$ . Calculated %: P 9.4

An attempt to distill the substance under reduced pressure (1-2 mm) was not successful, for at a bath temperature of about 150° decomposition set in.

Action of Acetaldehyde and Ethanethiol on O,O-Diisobutyl Phosphorodithioate

The reactants were O,O-diisobutyl phosphorodithioate (10 g), ethanethiol (2.5 g), and acetaldehyde (1.8 g) (cf. previous experiment). The reaction product decomposed when vacuum-distilled. Its purification consisted in a wash with water and drying over calcium chloride. The yield was 67.6%, and the compound had  $n_D^{20}$  1.5060;  $d_4^{20}$  1.0522.

Found %: P 9.50; 9.22  
 $C_{12}H_{27}S_3O_2P$ . Calculated %: P 9.4

SUMMARY

1. By the condensation of O,O-dialkyl phosphorodithioates with acetaldehyde and ethanethiol, five previously undescribed mixed esters of phosphorodithioic acid were synthesized.
2. A study was made of the insecticidal activity of the synthesized compounds with respect to the corn weevil.

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## ACTION OF HALOGENS ON ESTERS OF ANTIMONOUS ACID

B. A. Arbuzov and O. D. Samoilova

Addition reactions are characteristic of both phosphorous and arsenious esters, but whereas phosphorous esters are converted by halogens into quinquevalent phosphorous compounds by Arbuzov rearrangement [1], arsenious esters form only addition compounds with halogens [2].

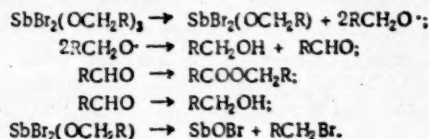
Antimonous esters have a pair of unshared electrons on the antimony atom and therefore should be capable of undergoing addition reactions to some extent.

The results of reactions that we have carried out show that triethyl and tributyl antimonites readily form addition products with chlorine and bromine.

Trialkoxystibine dihalides decompose when heated. Trialkoxystibine dichlorides decompose with the formation of the alkyl chloride, an ether, and antimony trichloride. Trialkoxystibine dibromides decompose in a more complicated fashion with formation of an ether, the alkyl bromide, an alcohol, an ester of a carboxylic acid, and antimony tribromide. The decomposition of trialkoxystibine dibromides in such a complex way is probably to be explained by the following properties of antimonous esters. We have shown previously that the Tishchenko ester condensation of aldehydes can be effected not only with aluminum and zinc alkoxides, but also, to a greater or less extent, with Zr, Ti, Sn<sup>IV</sup>, Sb<sup>III</sup>, and Sb<sup>V</sup> alkoxides; the alkoxides of these same metals are able to reduce aldehydes to alcohols [3].

In 1951 Nesmeyanov and coworkers found [4] that the action of halogens on tetraalkyl orthotitanates was accompanied by the elimination of an alcohol and an ester and the formation of dialkyldihalotitanium. The alcohol and ester were formed as a result of a peculiar disproportionation of the two alkoxy groups with the simultaneous formation of equimolecular amounts of alcohol and aldehyde. The latter underwent Tishchenko ester condensation in presence of the tetraalkyl orthotitanate.

In view of the tendency of the esters of antimony acids to promote the ester condensation of aldehydes and to reduce aldehydes to alcohols, we considered that it might be assumed that the complex decomposition of trialkoxystibine dibromides proceeds partially by the scheme proposed by Nesmeyanov for tetraalkyl orthotitanates:



The reducing properties of trialkoxystibine dibromides and their ability to effect the ester condensation of aldehydes was confirmed by us in experiments with benzaldehyde and isobutyraldehyde. In these reactions the corresponding alcohols and esters of the corresponding acids were isolated. When an alcoholic solution of benzaldehyde was boiled for a long time with triethoxystibine dichloride, the subsequent fractional distillation yielded only benzaldehyde.

### EXPERIMENTAL

#### Action of Chlorine on Triethyl Antimonite.

A flask containing 30 g of triethyl antimonite dissolved in chloroform (55 g) was cooled with snow, and dry chlorine was passed in until the weight increased by 7.5 g. In view of the instability of antimonous esters to hydrolysis, all reactions were carried out with exclusion of atmospheric moisture. When reaction was complete, chloroform was distilled off under somewhat reduced pressure from a water bath at 45-50°. After being recrystallized from ether, triethoxystibine dichloride melted at 50-53°.

Found: % Sb 36.67; 36.51; Cl 21.92; 22.08  
C<sub>6</sub>H<sub>15</sub>O<sub>3</sub>Cl<sub>2</sub>Sb. Calculated %: Sb 37.18; Cl 21.68

Triethoxystibine dichloride (30 g) was subjected to thermal decomposition in a flask carrying a Vigreux column and connected to traps.

When the oil-bath temperature reached 100° the crystalline substance melted, but no low-boiling fractions came over. At 145-150° vigorous decomposition set in. A low-boiling liquid collected in the trap; we did not succeed in determining the physical constants of this substance (it burned with a green flame). The yield of liquid was 2.1 g, or 7% of the amount taken. It appeared to be ethyl chloride, the reported boiling point of which is 12.5° [5]. Another liquid fraction, amounting to 6.8 g (22.8%) was collected. It had a boiling point of 34-36°, corresponding to diethyl ether.

After the thermal decomposition 18.8 g (60.2%) of a solid porous mass remained, and when this was distilled at 116-118° (10 mm), 2.6 g (60.2%) of a white crystalline substance was obtained. It had a melting point of 70-72°, corresponding to antimony trichloride, for which the literature [6] gives b.p. 223°, m.p. 73°.

Action of Bromine on Triethyl Antimonite. A chloroform solution of 30 g of triethyl antimonite was placed in a flask fitted with reflux condenser, and with snow cooling 18.6 g of bromine was carefully added. Each drop of bromine was immediately decolorized, but when the final addition was made decolorization was slower. Chloroform was then removed under somewhat reduced pressure from a water bath at 45-50°. The thick yellowish residue crystallized when dried in a vacuum desiccator. After being washed with ether and dried, the crystalline substance melted at 64-67°.

Found %: Sb 29.20; 29.70

$C_6H_{15}O_3Br_2Sb$ . Calculated %: Sb 29.21

This bromine-addition product (45 g) was subjected to thermal decomposition.

When the oil-bath temperature reached 110° the crystalline substance melted, but there was not a drop of low-boiling liquid on the walls of the flask. At 130-135° there was vigorous decomposition with frothing. The liquid fraction collected (19 g) boiled over the range 60-158°. A solid porous mass (21.5 g) remained in the flask. Fractionation of the liquid products yielded:

Fraction I,	b.p. 37-40°;	8.5 g
Fraction II,	b.p. 45-75°;	a few drops
Fraction III,	b.p. 77-79°;	4.1 g
Fraction IV,	b.p. 52-65° (14 mm);	2.9 g

Fraction I (8.5 g, b.p. 37-40°) was treated with a few drops of sulfuric acid in a flask fitted with a reflux condenser. From the resulting product 5.1 g of ethyl bromide, b.p. 38-39°, was isolated (the theoretically required amount is 11.7 g); about 3 g of diethyl ether was isolated.

Fraction II, b.p. 77-79°, had  $d_4^{20}$  0.8005. The melting point of the p-nitrobenzoic ester of this substance was 56-57°. The amount isolated was 4.1 g.

These results indicate that Fraction II was ethanol. The literature [7] gives b.p. 78.3°,  $d_4^{20}$  0.7893; p-nitrobenzoic ester, m.p. 57°.

Fraction IV was repeatedly distilled and yielded 2.2 g of a substance having b.p. 53-65° (14 mm);  $d_4^{20}$  1.5059;  $n_D^{20}$  1.4592; found MR 30.33; calculated MR 30.16. The substance irritated the mucous membrane of the eye. This fraction was ethyl bromoacetate. The literature [8] gives b.p. 168.7°;  $n_D^{15}$  1.4542;  $d_4^{15}$  1.5141 [8].

Action of Chlorine on Tributyl Antimonite. Dry chlorine was passed into a water-cooled flask containing 25 g of tributyl antimonite until the weight had increased by 5.2 g. A thick, yellowish liquid,  $d_4^{20}$  1.4073, was formed.

Found %: Sb 30.33; 29.91

$C_{12}H_{27}O_3Cl_2Sb$ . Calculated %: Sb 29.57

Tributoxystibine dichloride (27 g) was subjected to thermal decomposition in a flask fitted with a fractionating column. At an oil-bath temperature of 130-135°, vigorous decomposition set in. The following fractions were collected:

Fraction I,	b.p. 75-79°;	3.7 g
Fraction II,	b.p. 139-142°;	7.1 g

After the thermal decomposition, 14.2 g (52.6%) of a black, porous mass remained, and from this 2.12 g



of a white, crystalline substance was isolated. It had b.p. 114-115° (8 mm), and m.p. 70-72°. It was antimony trichloride.

After being redistilled, Fraction I had b.p. 77-78° and  $d_4^{20}$  0.8862; it was butyl chloride, for which the literature [9] gives b.p. 79° and  $d_4^{14}$  0.8972 [9].

After being redistilled, Fraction II had b.p. 46-47° (14 mm);  $d_4^{20}$  0.7814;  $n_D^{20}$  1.4054; it was dibutyl ether, for which the literature [10] gives b.p. 140.9° and  $d_4^{20}$  0.7841 [10].

**Action of Bromine on Tributyl Antimonite.** Tributyl antimonite (25 g) was treated cautiously under cooling with bromine (11.7 g). Each drop of bromine was immediately decolorized. The product was a thick, reddish liquid, which did not crystallize out when cooled. It had  $d_4^{20}$  1.7052.

Found %: Sb 24.80; 24.51

$C_{12}H_{27}O_3Br_2Sb$ . Calculated %: Sb 24.88

Tributoxystibine dibromide (36 g) was subjected to thermal decomposition. Vigorous decomposition began at an oil-bath temperature of 125-130°. Altogether, 18 g of a liquid fraction came over at 74-153°. The residue was 17.9 g (46.8%) of a black solid porous mass. This mass yielded 1.2 g of a white, crystalline substance melting at 95-97° and boiling at 165-168° (4 mm). It was antimony tribromide, for which the literature [6] gives m.p. 94°, b.p. 280°. The liquid fraction was fractionated through a Vigreux column and yielded:

Fraction I,	b.p. 74-82°;	1.1 g
Fraction II,	b.p. 85-104°;	2.2 g
Fraction III,	b.p. 113-117°;	10.2 g
Fraction IV,	b.p. 42-45° (12 mm);	2.1 g
Fraction V,	b.p. 56-62° (12 mm);	1.6 g

The fractions were redistilled. Fraction I (0.8 g, i.e. 2.2%) then boiled at 75-78° and had  $d_4^{20}$  0.8296; it gave a reddish precipitate with 2,4-dinitrophenylhydrazine. It was butyraldehyde, for which the literature [11] gives b.p. 75°,  $d_4^{20}$  0.8170;  $n_D^{20}$  1.38433. Fraction II (1.6 g, i.e. 4.4%; b.p. 101-104°,  $d_4^{20}$  1.2667, and  $n_D^{20}$  1.4314) was butyl bromide, for which the literature [9] gives b.p. 99.88° and  $d_4^{20}$  1.299. Fraction III (10.4 g, i.e. 28.9%; b.p. 114-117°,  $d_4^{20}$  0.8151, and  $n_D^{20}$  1.4012) was butyl alcohol, for which the literature [12] gives b.p. 116.7°,  $d_4^{20}$  0.8099, and  $n_D^{20}$  1.39909. Fraction IV (1.6 g, i.e. 4.4%; b.p. 43-44°/12mm,  $d_4^{20}$  0.7809;  $n_D^{20}$  1.4042) was dibutyl ether, for which the literature [10] gives b.p. 140.9° and  $d_4^{20}$  0.7841. Fraction V (0.9 g, i.e. 2.5%; b.p. 58-61°/12 mm,  $d_4^{20}$  0.8784, and  $n_D^{20}$  1.4086) was butyl butyrate: found MR 40.32; calculated MR 40.97. The literature [9] gives b.p. 164.8°,  $d_4^{20}$  0.8717 [9].

**Action of Triethoxystibine Dibromide on Benzaldehyde.** An alcoholic solution of 25 g of benzaldehyde (b.p. 67-68° at 11 mm) was boiled under reflux with 3 g of triethoxystibine dibromide for 25 hours. After two hours a white precipitate appeared in the reaction mixture, and the amount of this increased as the reaction proceeded. When the operation was complete the white precipitate was centrifuged off; it weighed 2.6 g. The alcoholic solution of reaction products was fractionally distilled. In a second distillation the following fractions were collected:

Fraction I,	b.p. 66-67° (11 mm);	14.3 g
Fraction II,	b.p. 86-87° (11 mm);	2.8 g
Fraction III,	b.p. 90-91° (11 mm);	2.4 g

The boiling point of Fraction I indicates that it was unchanged benzaldehyde (57.2% of the amount taken). Fraction II (2.8 g, i.e. 11.2%; b.p. 86-87°/11mm,  $d_4^{20}$  1.0428;  $n_D^{20}$  1.5342) was benzyl alcohol, for which the literature [13] gives b.p. 204.5-205.5°,  $n_D^{20}$  1.53955;  $d_4^{20}$  1.0429 [13].

Fraction III (2.4 g, i.e. 9%; b.p. 90-91°/11 mm,  $d_4^{20}$  1.0497, and  $n_D^{20}$  1.5049) was ethyl benzoate, for which the literature [14] gives b.p. 211.2°,  $d_4^{15}$  1.0509, and  $n_D^{15}$  1.5079.

After the first fractionation there was a black crystalline residue. Recrystallization from ligroin yielded white crystals, which yellowed somewhat when exposed to air. Its melting point, which was 63-64° after several recrystallizations, indicates that it was phenyl m-l monobenzoate, for which the literature [15] gives m.p. 65°. The yield of crude product was 1.2 g.

**Action of Tributoxystibine Dibromide on Isobutyraldehyde.** A mixture of 30 g of isobutyraldehyde and 5 g of tributoxystibine dibromide was prepared in a sealed tube. Reaction began at room temperature, so that the reaction mixture became appreciably warm, the bromine color disappeared, and a white precipitate appeared. The

sealed tube was heated for six hours at 90-100°. The precipitate was centrifuged off, and the supernatant liquid was fractionally distilled. Redistillation yielded the following fractions:

Fraction I,	b.p. 64-66°; 20.2 g
Fraction II,	b.p. 106-112°; 1.8 g
Fraction III,	b.p. 114-148°; 3.5 g
Residue	5 g

The boiling point of Fraction I indicated that it was unchanged isobutyraldehyde. Fraction II (b.p. 106-112°,  $d_4^{20}$  0.8034) was isobutyl alcohol, for which the literature [16] gives b.p. 108.39° and  $d_4^{20}$  0.8003. Fraction III (b.p. 144-148°,  $d_4^{20}$  0.8728) was isobutyl isobutyrate, for which the literature [17] gives b.p. 146.6° and  $d_4^{20}$  0.87495.

Action of Tributoxystibine Dichloride on Benzaldehyde. An alcoholic solution of 30 g of benzaldehyde was refluxed for 25 hours with 3 g of tributoxystibine dichloride. During this time no changes were observed in the reaction mixture. Fractionation of the mixture gave the original substances.

#### SUMMARY

1. Chlorine and bromine readily form addition products with antimonous esters.
2. The course of the thermal decomposition of trialkoxystibine dibromides is more complex than that of trialkoxystibine dichlorides. Trialkoxystibine dichlorides decompose with formation of an alkyl chloride, an ether, and antimony trichloride, while trialkoxystibine dibromides yield an alkyl bromide, an ether, an alcohol, and a carboxylic ester.
3. Trialkoxystibine dibromides are able to promote the Tishchenko ester condensation of aldehydes, and they are also able to reduce aldehydes.

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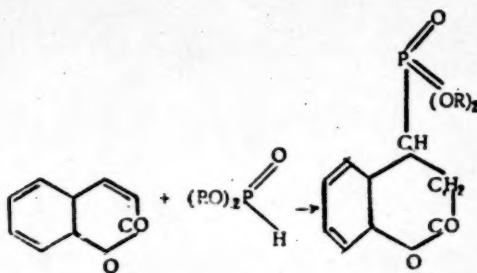
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# SYNTHESIS OF PHOSPHONIC ESTERS CONTAINING HETEROCYCLIC RADICALS COMMUNICATION 5. PHOSPHONIC ESTERS CONTAINING A HYDROCOUMARIN RADICAL

B. A. Arbuzov and V. M. Zoroastrova

This paper is one of a series on the synthesis and properties of phosphonic esters containing heterocyclic groups [1, 2, 3, 4].

We have effected the syntheses of phosphonic esters in which phosphorus is attached to a heterocycle by the method discovered by Arbuzov and Pudovik [5] who carried out the addition of diethyl hydrogen phosphite to chloromethoxypentenes, and further developed in investigations by Pudovik. In presence of a sodium alkoxide, an alkyl diphosphite will add to an  $\alpha, \beta$ -unsaturated ketone with formation of esters of  $\gamma$ -keto phosphonic acids. It would be expected that coumarin and its homologs would undergo a similar addition reaction with formation of esters of "hydrocoumarin-4-ylphosphonic acid":



The experiments that we have now carried out show that dialkyl phosphites add to coumarin and to 4-methylcoumarin (in presence of sodium alkoxides as catalysts) with formation of hydrocoumarinylphosphonic esters. Analogy with the addition products formed by dialkyl phosphites with  $\alpha, \beta$ -unsaturated ketones indicated the position taken up by the phosphonic grouping in the hydrocoumarin nucleus. Addition of the dialkyl phosphite at the carbonyl group or with cleavage of the lactone ring is much less probable.

To check these possibilities we attempted to bring about the addition of diethyl phosphite to hydrocoumarin, and negative results were obtained, the original substances being recovered unchanged even when severe conditions were used. On the basis of these results it may be considered that addition of dialkyl phosphites occurs at the  $C=C$ -bond.

Hydrolysis of the hydrocoumarin-4-yl- and 4-methylhydrocoumarin-4-yl-phosphonic esters with hydrochloric acid yielded, respectively, hydrocoumarin-4-ylphosphonic acid, m.p. 218-220° and 4-methylhydrocoumarin-4-ylphosphonic acid, m.p. 192-193°. The constants and yields of the compounds obtained are given in the table.

Unusual ease of reaction with diethyl phosphite was shown by 3-acetylcoumarin. Thus, when 3-acetylcoumarin and diethyl phosphite were heated with a little sodium ethoxide at 120°, reaction was complete in two hours. The product was a crystalline substance melting at 146-149° (from methanol) and corresponding in analysis to the product of the addition of one molecule of diethyl phosphite to one molecule of acetylcoumarin.

We did not succeed in obtaining a phenylhydrazone from the addition product formed by diethyl phosphite with 3-acetylcoumarin, although acetylcoumarin itself reacts readily with phenylhydrazine to form a crystalline phenylhydrazone melting at 182-183°. The possibility that diethyl phosphite added at the carbonyl group of the acetyl radical cannot be excluded, and the formula given for this compound in the table must be regarded as tentative.

It is notable that the determined molecular refraction values differ greatly from the values calculated theoretically. The discrepancy is almost constant at 1-1.3 units.

The compounds numbered 2 and 7 in the table were tested on corn weevils for insecticidal activity, but this was found to be very low.

TABLE

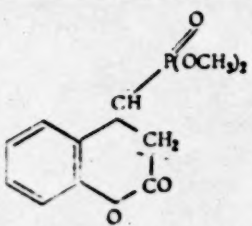
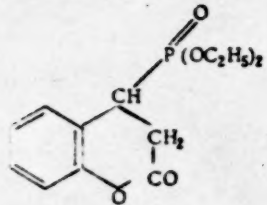
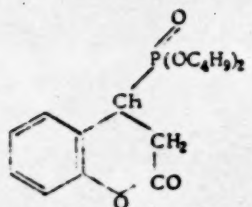
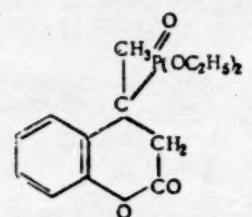
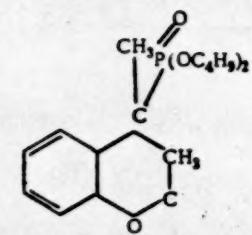
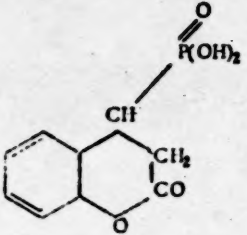
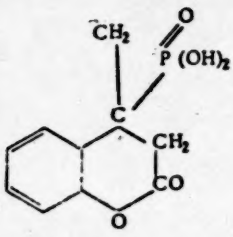
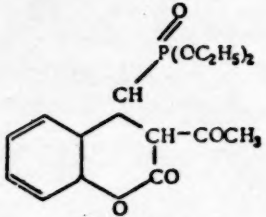
Formula	B.p. in °C (p in mm)	$d_4^{20}$	$n_D^{20}$	MR		Yield (%)
				Found	Calculated	
	190-195 (7)	1.3038	1.5303	60.70	59.71	19.6
	200-203 (6-6.5)	1.2255	1.5150	60.91	68.93	17
	223 (7-7.5)	1.1302	1.5015	88.75	87.42	18.3
	196-198 (5)	1.2131	1.5205	74.77	73.57	24
	215-218 (5-5.5)	1.1273	1.5070	93.42	92.14	24.3



TABLE (Continued)

Formula	B.p. in °C (p in mm)	$d_4^{20}$	$n_D^{20}$	MR		Yield (%)
				Found	Calculated	
	M.p 218-220 (from a mixture of ethyl and butyl acetates)					
	M.p 192-193 (colorless needles from ethyl acetate)					
	M.p 146-149°					

We carried out some experiments on the reaction of diethyl phosphorodithiophate with coumarin, but no positive results were obtained. It was evident that reaction did occur under certain conditions, but we were unable to isolate an individual product because decomposition occurred during distillation at reduced pressure (10-14mm). Positive results were again not obtained for the reaction of diethyl phosphite with 2,6-dimethyl-4H-pyran-4-one, no addition products being obtained under similar reaction conditions.

## EXPERIMENTAL

### 1. Reaction of Dimethyl Phosphite with Coumarin

Equivalent amounts of coumarin (5.8 g) and dimethyl phosphite (4.4 g) were placed in an Arbuzov flask. The dissolution of the coumarin in the dimethyl phosphite was accompanied by a fall in temperature from 19° to 15°. After the addition of ten drops of a concentrated solution of sodium methoxide in methanol, almost the whole of the coumarin dissolved and formed a clear solution. This solution was heated in an oil bath at 110-120° for 20 hours. The product was a thick liquid having the color of weak tea. Vacuum distillation after the addition of a few drops of glacial acetic acid gave the following fractions:

- B.p. 65-72° (15 mm); 2 g
- B.p. 135-155° (7mm) 2 g (solidified in the condenser)
- B.p. 155-195° (7mm); 2.8 g

Redistillation of Fraction III gave the fractions:

- B.p. 143-190° (7mm); 0.3 g
- B.p. 190-195° (7mm); 2 g (19.6%)

The second of these fractions was investigated in greater detail and found to have  $n_D^{20}$  1.5303;  $d_4^{20}$  1.3038; found MR 60.70; calculated MR 59.71. It was a very viscous liquid, soluble in benzene and ether, but insoluble in water.

Found %: P 11.63

$C_{11}H_{13}O_5P$ . Calculated %: P 12.10

**Hydrolysis of the Product.** The product (0.8 g) was heated with 10 ml of 1:1 hydrochloric acid in a sealed tube at 100° for five hours. The contents of the tube were evaporated on a water bath with addition of water from time to time until the hydrochloric acid had been completely removed. The crystalline product was recrystallized from a 1:4 mixture of ethyl and butyl acetates. Fine colorless needles were obtained, and these became pale gray when heated to 200°, and then melted to a brown liquid at 218-220°. The substance is soluble in water, methanol, ethanol, acetone, and acetic esters.

Found %: P 13.08

$C_9H_9O_5P$ . Calculated %: P 13.59

## 2. Reaction of Diethyl Phosphite with Coumarin

Reaction was between 7 g of coumarin (m.p. 68-70°) and 7.4 g of diethyl phosphite. When the coumarin was added to the diethyl phosphite, slight cooling (by 2-3°) was observed. Sodium ethoxide solution (10 drops) was added (there was no rise of temperature), and the mixture was heated in an oil bath at 120° for six hours. When the mixture was cooled, coumarin crystals were precipitated. More sodium ethoxide solution (10 drops) was added, and heating was continued at 125-135° for six hours. The mixture was then neutralized with glacial acetic acid and vacuum-distilled. The fractions obtained were:

B.p. 67-71° (10 mm); 3.6 g

B.p. 145-155° (10 mm); 3.0 g (solidified in the condenser; it was found to be unchanged coumarin)

B.p. 165-198° (4.5 mm); 4.2 g

Residue in flask 3 g

Refractionation of Fraction III yielded 2.5 g (about 17%) of a substance having b.p. 200-203° (6-6.5 mm);  $n_D^{20}$  1.5150;  $d_4^{20}$  1.2255; Found MR 69.91; Calculated MR 68.93. It was a colorless oil, soluble in organic solvents, but insoluble in water.

Found % P 11.03; 11.39

$C_{13}H_{17}O_5P$ . Calculated %: P 10.91

Analysis indicated that the substance was the product formed by the addition of one molecule of diethyl phosphite to one molecule of coumarin.

**Hydrolysis of the Product.** A sealed tube containing 1 g of the product and 10 ml of 1:1 hydrochloric acid was heated in a boiling water bath for 6 hours 30 minutes. Evaporation of water and removal of hydrochloric acid on a water bath left a crystalline substance (about 1 g), which was dirty pink in color. It was recrystallized from a mixture of ethyl and butyl acetates, the solutions being treated with activated charcoal. The pure acid melted at 218-220°.

## 3. Reaction of Dibutyl Phosphite with Coumarin

A mixture of 3.5 g of coumarin and 4.7 g of dibutyl phosphite was prepared in an Arbuzov flask, when dissolution occurred with a fall in temperature of 3°. After the addition of 8-10 drops of a saturated solution of sodium butoxide in butyl alcohol, the mixture was heated for 6.5 hours at 130-140° and for 10 hours at 145-155°. The contents of the flask then consisted of a viscous liquid having the color of weak tea. The material was neutralized with glacial acetic acid and vacuum-distilled. The fractions obtained were:

B.p. 108-132° (8 mm); 2.4 g (mixture of original substances)

B.p. 132-145° (8 mm); 1.1 g (solidified in condenser; mainly coumarin)

B.p. 223° (7-7.5 mm); 1.5 g (18.3%)

Fraction III, a thick yellowish liquid, was similar in properties to the product of the preceding experiment; it had  $n_D^{20}$  1.5015;  $d_4^{20}$  1.1302; Found MR 88.75; Calculated MR 87.42.

Found %: P 9.52; 9.58

$C_{17}H_{23}O_5P$ . Calculated %: P 9.11

**Hydrolysis of the Product.** The product (0.7 g) was refluxed with 10 ml of 1:1 hydrochloric acid for three hours. After the usual treatment, the hydrolysis product was recrystallized from a 4:1 mixture of ethyl and butyl acetates. Colorless crystals were obtained which were identical with those obtained previously by hydrolysis of the

addition products formed by dimethyl phosphite and by diethyl phosphite with coumarin (m.p. 218-220°; mixture test, m.p. 218-219.5°).

#### 4. Reaction of Diethyl Phosphite with 4-Methylcoumarin

4-Methylcoumarin was prepared, as previously described [6], by the condensation of phenol with acetoacetic ester. A mixture of 9 g of 4-methylcoumarin and 7.7 g of diethyl phosphite was heated with 10 drops of alcoholic sodium ethoxide for six hours in a water bath and then for four hours at 120-125°. After the addition of a few drops of glacial acetic acid, the mixture was vacuum-fractionated and yielded:

B.p. 65-68° (9 mm); 4.3 g

B.p. 160-172° (5 mm); 2.3 g (solidified in condenser; methylcoumarin)

B.p. 172-200° (5 mm); 7 g

There was a thick brown resinous residue. Fraction III was redistilled and yielded:

B.p. 174-196° (5 mm); in very small amount

B.p. 196-198° (5 mm); (with slight decomposition)

Fraction II was a thick oil, insoluble in water, but readily soluble in ether, benzene, acetone, and other organic solvents. It had  $n_D^{20}$  1.5205;  $d_4^{20}$  1.2131; Found MR 74.77; Calculated MR 73.57. The yield was 4 g (24%).

Found %: P 10.55; 10.35

$C_{14}H_{12}O_5P$ . Calculated %: P 10.39

Hydrolysis of the Product. A sealed tube containing 2 g of the product and 15 ml of 1:1 hydrochloric acid was heated for six hours in a water bath. The contents of the tube were evaporated on the water bath, water being added frequently until the whole of the hydrochloric acid had been removed. When the whole of the water was evaporated away, the mass crystallized, 1.9 g of dirty-red crystals being obtained. After two crystallizations from acetic acetate with simultaneous application of activated charcoal, colorless needles having a double melting point were obtained: the crystals became "wet" when heated to 108-110°, resolidified when heated further (120-125°), and finally melted at 192-193°. The substance is soluble in water and in alcohol, and it dissolves when heated with ethyl or butyl acetate or with acetone; it is sparingly soluble in benzene and ether, and is insoluble in petroleum ether.

Found %: P 12.56; 12.60

$C_{13}H_{11}O_5P$ . Calculated %: P 12.80

#### 5. Reaction of Dibutyl Phosphite with 4-Methylcoumarin

A mixture of 3.2 g of 4-methylcoumarin and 3.88 g of dibutyl phosphite was heated at 135-140° with a few drops of a solution of sodium butoxide in butyl alcohol for 6 hours 30 minutes. After the addition of 5-6 drops of glacial acetic acid, the product was vacuum-distilled. After a second distillation 1.7 g (24.3%) of a fraction boiling with slight decomposition at 215-218° (5-5.5 mm) was obtained. It had  $n_D^{20}$  1.5070;  $d_4^{20}$  1.1283; Found MR 93.42; Calculated MR 92.14. It was a viscous liquid, soluble in organic solvents.

Found % P 8.26

$C_{18}H_{27}O_5P$ . Calculated %: P 8.75

Hydrolysis of the Product. The product (0.7 g) was refluxed with 10 ml of 1:1 hydrochloric acid until the oil present disappeared (three hours). Evaporation on a water bath yielded a solid substance, which was crystallized from ethyl acetate (colorless needles). Its melting point was not depressed by admixture of the product of the hydrolysis of the corresponding ethyl ester.

#### 6. Reaction of Diethyl Phosphite with Acetylcoumarin

Acetylcoumarin (m.p. 123°, from alcohol) was prepared by the condensation of salicylaldehyde with acetoacetic ester in presence of piperidine [7]. A mixture of equimolecular amounts of acetylcoumarin (9 g) and diethyl phosphite (6.6 g) with 8 drops of a saturated alcoholic solution of sodium ethoxide was heated in an Arbuzov flask in an oil bath at 120°. After two hours the flask was cooled, when its contents solidified completely to a very dense brown mass (in order to remove it it was necessary to break the flask). The product was recrystallized from absolute methanol with the application of activated charcoal, and crystals melting at 146-149° were obtained. We did not succeed in obtaining crystals having a sharper melting point, probably owing to the occurrence of transesterification during crystallization from methanol. When the product was melted it would not resolidify, but remained as a viscous liquid. The use of other solvents for the purpose of crystallization did not give the desired results. The substance was soluble in hot



alcohol and slightly soluble in hot water; it was readily soluble in benzene and ethyl acetate, but insoluble in petroleum ether.

Found %: P 9.85; 9.74  
 $C_{15}H_{15}O_6P$ . Calculated %: P 9.50

An attempt to prepare the phenylhydrazone by the action of phenylhydrazine in glacial acetic acid did not give positive results, though, under the same conditions, pure acetylcoumarin readily gave a phenylhydrazone, m.p. 182-183°.

Hydrolysis of the Product. The substance (2 g) was refluxed with 18 ml of 1:1 hydrochloric acid for three hours. The clear solution was evaporated in a dish on a water bath until the hydrochloric acid was removed completely. When cooled, the contents of the dish solidified to a very hard glossy mass, which we were unable to recrystallize in spite of attempts with all of the usual solvents. The product was ground in a mortar, when it formed a dirty-violet powder. It did not change when heated to 125°, and then turned red as the temperature was raised further.

Found %: P 12.03; 12.05  
 $C_{11}H_{11}O_6P$ . Calculated %: P 11.47

## 7. Experiments with Hydrocoumarin

Hydrocoumarin was prepared by the reduction of coumarin with sodium amalgam and distillation of the melilic acid obtained [8]. It had b.p. 269-271° and  $n_D^{20}$  1.5595; the literature gives b.p. 272°. Dihydrocoumarin was identified by the preparation of its dibromide, m.p. 104-106° (the literature gives 106°).

Experiment 1. A mixture of 5 g of hydrocoumarin and 4.65 g of diethyl phosphite was heated in an Arbuzov flask with 10 drops of sodium ethoxide solution at 125-135° for 17 hours. After three fractionations the original substances were recovered. No high-boiling fractions were detected.

Experiment 2. A mixture of 9.7 g of hydrocoumarin and 9.04 g of diethyl phosphite was heated with 15 drops of sodium ethoxide solution at 150-155° for 10.5 hours. After several fractionations 7.5 g of diethyl phosphite (b.p. 75-80°/14 mm) and 6.7 g of hydrocoumarin (b.p. 268-272°;  $n_D^{20}$  1.5590) were obtained. There was a very small amount of thick brown resinous residue in the distillation flask.

## 8. Experiments with 2,6-Dimethyl-4H-pyran-4-one

Experiment 1. A mixture of equimolecular amounts of 2,6-dimethyl-4H-pyran-4-one (4.4 g) and diethyl phosphite (4.9 g) was heated in a water bath with 12-15 drops of a saturated solution of sodium ethoxide for 7.5 hours. When the mixture was cooled, crystals of the pyrone came down. The mixture was heated further for 14 hours at 130°. The contents of the flask then consisted of a thick brown resinous liquid, the distillation of which yielded:

B.p. 75-80° (10 mm); 2.5 g  
B.p. 80-125° (10-14 mm)

Fraction II partially crystallized out, and 1.8 g of 2,6-dimethyl-4H-pyran-4-one was obtained. When the temperature was raised further, decomposition set in and the pressure rose to 16 mm. In the distillation flask there remained a glossy black carbonaceous product (2 g) reminiscent of anthracite.

Experiment 2. A mixture of 4.85 g of 2,6-dimethyl-4H-pyran-4-one and 5.4 g of diethyl phosphite was heated with 12 drops of sodium ethoxide solution at 110-120° for the duration of four daily sessions (about 30 hours). When the mixture was cooled, crystals of the pyrone came down (2.8 g; m.p. 131-132°). Vacuum distillation gave:

B.p. 68-78° (8-7.5 mm); 4 g  $n_D^{20}$  1.4075 (impure diethyl phosphite)  
B.p. 108-115 (8-7.5 mm); in small amount (2,6-dimethyl-4H-pyran-4-one)

There was a black residue in the flask. The reaction did not go.

## 9. Reaction of Diethyl Phosphorodithioate with Coumarin

Experiment 1. A mixture of 4.1 g of diethyl phosphorodithioate and 3.1 g of coumarin was heated in a water bath for six hours. When the reaction mixture was cooled, yellow crystals came down, and these were found to be coumarin contaminated with sulfur (m.p. 68-70°). An addition of 10 drops of sodium ethoxide solution was made, and heating was continued for a further six hours. Fractionation of the mixture under reduced pressure yielded the original substances; there were no high-boiling fractions. The reaction did not go.



**Experiment 2.** A mixture of 7.3 g of coumarin, 9.3 g of diethyl phosphorodithioate, and 15 ml of dry benzene was heated in a sealed tube at 120-125° for seven hours. The tube was found to contain an intensely black liquid, which was fractionated. The products isolated were 3 g of diethyl phosphorodithioate, b.p. 109-112° (9 mm) and 4 g of a fraction boiling at 145-148° (9 mm), which solidified in the condenser to yellow crystals (coumarin contaminated with sulfur). Further heating resulted in decomposition. There was a resinous residue.

**Experiment 3.** A mixture of 7.3 g of coumarin and 9.3 g of diethyl phosphorodithioate was refluxed at 150° for 15 minutes. The contents of the flask became yellow. Distillation yielded 1.5 g of a fraction having b.p. 37-42° and  $n_D^{20}$  1.4368, which correspond to ethanethiol (reported values: b.p. 37°,  $n_D^{20}$  1.4305). Further distillation under reduced pressure gave the following fractions:

B.p. 115-126° (14 mm); a small amount of diethyl phosphorodithioate.

B.p. 126-152° (14 mm); yellow liquid, which partially crystallized, yielding coumarin. m.p. 67-69°.

B.p. 152-155° (14 mm); 1.3 g coumarin.

At the end of the distillation decomposition set in. Much resin remained in the distillation flask.

#### SUMMARY

1. In presence of sodium alkoxides, dialkyl phosphites add to coumarin and to 4-methylcoumarin with formation of esters of hydrocoumarin-4-yl- and 4-methylhydrocoumarin-4-yl-phosphonic acids, respectively.

2. Experiments on the addition of diethyl phosphite to 2,6-dimethyl-4H-pyran-4-one and of diethyl phosphorodithioate to coumarin did not give positive results.

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# REACTIONS OF MERCAPTO AMINO ACIDS

## COMMUNICATION 9. SYNTHESIS OF $\alpha$ -ACYLAMINO $\beta$ -THIOLACTONES

I. L. Knunyants, O. V. Kildisheva, and E. Ya. Pervova

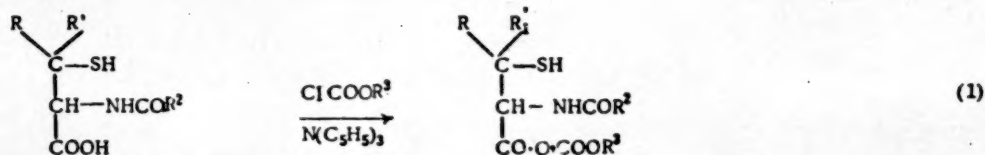
In spite of the great progress that has been made in the synthesis of polypeptides having a predetermined sequence of amino-acid residues, there are still great difficulties in the way of the preparation of mixed polyamides in which the chain is built up from mercapto amino acids as well as the usual  $\alpha$ -amino acids. Only very few such polypeptides have been synthesized. Still less study has been devoted to polypeptides derived entirely from mercapto amino acids. The following are known: L-cystyl-L-cystine, prepared by the hydrolysis of the corresponding piperazinedione [1]; polycystine, prepared by heating L-cystine bis-N-carboxyanhydride [2]; poly-S-benzylcysteine [3] prepared from S-benzyl-L-cysteine N-carboxyanhydride; and L-methionyl-L-methionine and L-methionyl-L-methionyl-L-methionine, prepared by the azide method from N-(benzyloxycarbonyl) methionine [4].

The only known dipeptide containing free thiol groups is cysteinylcysteine. Polypeptides derived from 3,3-dimethylcysteine and other mercapto amino acids have not been studied.

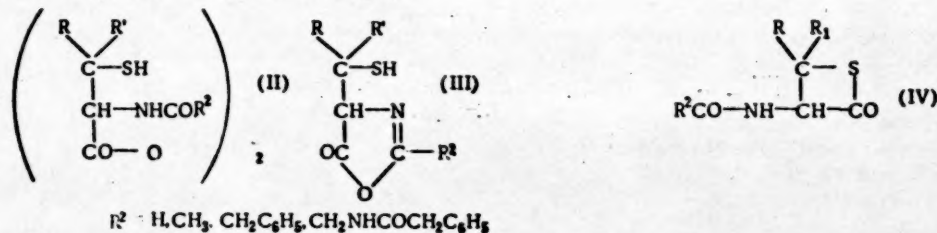
Complications arise in the synthesis of such polypeptides owing to the high reactivity of mercapto amino acids, in which not only the amino, but also the thiol groups must be blocked before the compounds can be applied in the peptide synthesis. The removal of the protective groups from the resulting polypeptides can be effected only with difficulty. The usual method of blocking a thiol group is benzylation, and the benzyl group may be removed from the polypeptide by reduction with sodium in liquid ammonia. As shown in the preceding communications, in the case of 3,3-dimethylcysteine blocking the amino groups (acylation) presents no difficulty and can be readily carried out even without previous protection of the thiol group [5].

Among the general methods of synthesizing peptides (from piperazinediones, acid chlorides, azides, etc.), the one most widely applied in recent times is the method of acylation with the aid of mixed anhydrides and N-carboxyanhydrides of amino acids, and most frequently mixed anhydrides of acylamino acids with carbonic monoesters are used. An illustration of the possibilities of this method is provided by the synthesis of cyclo-D-leucylglycylglycine in 37% yield [6], and also by the synthesis of a cyclic octapeptide [7], which was found to be identical in its chemical and physical properties with the natural hormone oxytocin.

The application of this method to mercapto acylamino acids must inevitably lead to the formation of the mixed anhydride (I):

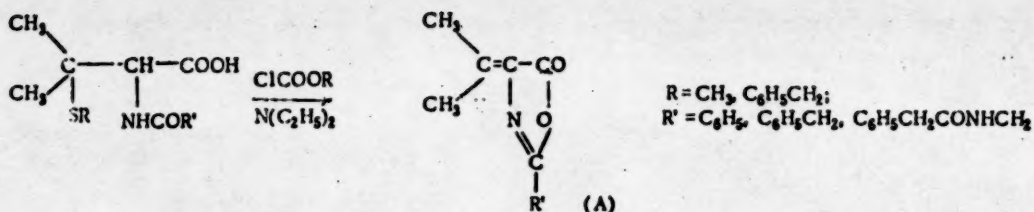


The further transformations of the mixed anhydride (I), apart from possible symmetrization (II), may proceed in two competing directions, with formation of a five-membered system - the oxazolinone (III), and with formation of a four-membered system - the  $\beta$  thiolactone (IV):



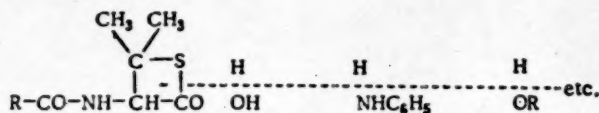






Thus, from N-benzoyl-S-benzyl-, S-benzyl-N-phenylacetyl-, and S-methyl-N-phenacetyl-3,3-dimethylcysteines, the corresponding unsaturated oxazolinones were prepared by the action of chloroformic ester in presence of trimethylamine.

A study of the properties of thiolactones showed that these compounds are stable: their hydrolysis by water proceeds very slowly at room temperature, only 50% of the thiolactone being converted into the N-acyl-3,3-dimethylcysteine in the course of two weeks. When warmed with water or bicarbonate solution, thiolactones are readily hydrolyzed to the corresponding acids, and the solution then again gives the ferric chloride reaction for the thiol group. When thiolactones are heated with alcohols, esters of N-acyl-3,3-dimethylcysteine are formed. They react with aniline even at room temperature, with formation of anilides. Alcoholysis in presence of lead acetate yields the corresponding mercaptides:



#### EXPERIMENTAL

General Method for the Preparation of  $\beta$ -Thiolactones from N-Acyl-3,3-dimethylcysteines. A solution of one molecular proportion of the N-acyl-3,3-dimethylcysteine and two molecular proportions of triethylamine in dry chloroform was cooled to  $-10^\circ$  and stirred while a cooled solution of 1.5 molecular proportions of isobutyl chloroformate in dry chloroform was added (the temperature must not be allowed to rise above  $-6^\circ$ ). The reaction mixture was kept at  $-5^\circ$  until there was no longer a reaction for the thiol group (5-10 minutes), and the temperature was then allowed to rise to that of the room (there was a vigorous evolution of carbon dioxide, even at  $0^\circ$ ). The solution was evaporated under reduced pressure, the dry residue was rubbed out with ether, and the substance was filtered off, washed well with water, dried in a vacuum desiccator over phosphoric oxide, and crystallized.

Anilide of N-Formyl-3,3-dimethylcysteine. The above-described preparation was carried out on 0.17 g (0.001 mole) of N-formyl-3,3-dimethylcysteine up to the stage of the disappearance of the reaction for the thiol group with ferric chloride and, without isolation of the thiolactone, a solution of 0.09 g (0.001 mole) of aniline in dry chloroform was then added at  $-5^\circ$ . The reaction mixture was set aside at room temperature overnight. On the next day the solution was evaporated to dryness and the residue was washed successively with bicarbonate solution, water, dilute hydrochloric acid, and water. It was dried over phosphoric oxide in a vacuum desiccator. The product was 0.1 g of the anilide of N-formyl-3,3-dimethylcysteine, m.p.  $165-169^\circ$  (from absolute alcohol).

Found %: N 11.3

$\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_2\text{S}_2$ . Calculated %: N 11.3

Anilide of N-Acetyl-3,3-dimethylcysteine. A solution of 0.25 g (0.0014 mole) of N-acetyl-3,3-dimethylcysteine  $\beta$ -thiolactone in 0.5 g (0.005 mole) of aniline was prepared. The solution was set aside at room temperature overnight, and on the next day the precipitate that had formed was filtered off and washed successively with 2 N HCl, water, bicarbonate solution, and again water. The product was 0.38 g (a quantitative yield) of the anilide of N-acetyl-3,3-dimethylcysteine, m.p.  $193-195^\circ$  (from alcohol).

Found %: C 58.45; H 6.80; S 11.92; N 10.71

$\text{C}_{13}\text{H}_{18}\text{O}_2\text{N}_2\text{S}$ . Calculated %: C 58.64; H 6.76; S 12.03; N 10.52

3,3-Dimethyl-N-phenacetyl-3,3-dimethylcysteine  $\beta$ -Thiolactone\*. A solution of 0.97 g (0.003 mole) of 3,3-dimethyl-

\* The first suggestion that a  $\beta$ -thiolactone is formed in the reaction of acetic anhydride with 3,3-dimethyl-N-phenacetyl-3,3-dimethylcysteine was made by Sus[9], but the substance that he isolated melted at  $143^\circ$ .

N-phenacetyl cysteine and 0.6 g (0.006 mole) of triethylamine in 20 ml of dry chloroform was cooled to  $-10^{\circ}$  and stirred while a cooled solution of 0.4 g (0.003 mole) of isobutyl chloroformate in dry chloroform was added. A copious precipitate of the thiolactone formed immediately, and an immediate ferric chloride test for thiol groups was negative. The precipitate was filtered off, washed with water, and dried in a vacuum desiccator over phosphoric oxide. The product was 0.9 g (a quantitative yield) of 3,3-dimethyl-N-phenacetyl cysteine  $\beta$ -thiolactone, which melted with decomposition at  $191-194^{\circ}$  (from absolute ethanol). The thiolactone was not soluble in water, ether, chloroform, benzene, ethyl acetate, and dioxane, and it was poorly soluble in alcohol.

Found %: C 59.1; H 5.80; S 10.60; N 9.20

$C_{15}H_{18}O_3N_2S$ . Calculated %: C 58.82; H 5.80; S 10.45; N 9.15

b) A solution of 0.62 g (0.003 mole) of phenacetic acid and 0.3 g (0.003 mole) of triethylamine in 10 ml of dry chloroform was cooled to  $-10^{\circ}$  and stirred while 0.84 g (0.006 mole) of isobutyl chloroformate was added. After 5-10 minutes a cooled solution of 0.45 g (0.003 mole) of 3,3-dimethylcysteine in 3 ml of N NaOH (0.002 mole) was added, and the mixture was stirred vigorously with cooling for 15 minutes (a copious precipitate of thiolactone formed); stirring was continued for a further 30 minutes at  $20^{\circ}$ . The precipitate was filtered off, washed with chloroform, and dried in a vacuum desiccator over phosphoric oxide. The product was 0.45 g (50%) of 3,3-dimethyl-N-phenacetyl cysteine  $\beta$ -thiolactone, m.p.  $170-181^{\circ}$ , raised by recrystallization from alcohol to  $190-192^{\circ}$ . A mixture test with the substance obtained in the preceding experiment showed no depression.

When the alkaline solution was acidified, 0.1 g of 3,3-dimethyl-N-phenacetyl cysteine was obtained.

#### Reactions of 3,3-Dimethyl-N-phenacetyl cysteine $\beta$ -Thiolactone.

a) With lead acetate. The thiolactone (0.5 g, i.e. 0.0016 mole) was dissolved in methanol at  $40^{\circ}$  and 0.5 g (0.0015 mole) of lead acetate was added. The mixture was refluxed for eight hours, and the black precipitate formed was filtered off (60 mg, i.e. 15% of lead sulfide). The filtrate was evaporated under reduced pressure at room temperature. The yellow residue was well washed with ether, alcohol, and then water; it was dried over phosphoric oxide in a vacuum desiccator. The product was 0.5 g of the methyl ester of 3,3-dimethyl-N-phenacetyl cysteine in the form of its lead mercaptide. Evaporation of the ether-alcohol mother liquor yielded a further 0.1 g of the mercaptide. The total yield of mercaptide was 0.6 g (85%). It was crystallized from dioxane and then from absolute alcohol. After being dried over phosphoric oxide in a vacuum, it melted with decomposition at  $150^{\circ}$  (partial liquefaction occurred at  $110^{\circ}$ ).

Found %: C 43.57; H 4.94; N 5.80;  $CH_3O$  7.52

$C_{12}H_{16}O_3N_2S_2Pb$ . Calculated %: C 43.58; H 4.76; N 6.35;  $CH_3O$  7.03

b) Pyrolysis. 3,3-Dimethyl-N-phenacetyl cysteine  $\beta$ -thiolactone was heated at a temperature close to its melting point ( $190^{\circ}$ ) at a residual pressure of 2 mm for 20-30 minutes (until decomposition ceased). The residue was rubbed out with ether and recrystallized from ethyl acetate.

The product was a crystalline substance melting at  $157-158^{\circ}$  (N-2-methylpropenylphenacetamide).

Found %: C 68.18; H 7.42; N 11.22

$C_{14}H_{18}N_2O_2$ . Calculated %: C 68.29; H 7.32; N 11.38

In order to prove that this was N-2-methylpropenylphenacetamide, it was hydrolyzed with 2 N HCl in presence of 2,4-dinitrophenylhydrazine. The precipitate that formed was filtered off and crystallized from alcohol. The product was a hydrazone melting at  $178-180^{\circ}$ , and there was no depression in a mixture test with the 2,4-dinitrophenylhydrazone of isobutyraldehyde.

#### 4-Isopropylidene-2-phenyl-2-oxazolin-5-one.

a) From N-benzoyl-3,3-dimethylcysteine. A solution of 0.54 g (0.002 mole) of N-benzoyl-3,3-dimethylcysteine and 0.4 g (0.004 mole) of triethylamine in 5 ml of dry chloroform was cooled to  $-10^{\circ}$ , and a cooled solution of 0.28 g (0.002 mole) of isobutyl chloroformate was added. After 15 minutes the temperature was raised to that of the room and the solution was evaporated to dryness. The residue was extracted with ether; the yield of  $HClN(C_2H_5)_3$  was quantitative. The ether solution was evaporated at room temperature, and the oily residue was treated with a small amount of alcohol. The product was 0.28 g (70%) of 4-isopropylidene-2-phenyl-2-oxazolin-5-one, m.p.  $94-95^{\circ}$ , undepressed by admixture of 4-isopropylidene-2-phenyl-2-oxazolin-5-one prepared by another method.

b) From N-benzoyl-S-benzyl-3,3-dimethylcysteine. A solution of 0.34 g (0.001 mole) of N-benzoyl-S-benzyl-3,3-dimethylcysteine and 0.1 g (0.001 mole) of triethylamine in 5 ml of dry chloroform was cooled to  $-10^{\circ}$ ,

and a cooled solution of 0.14 g (0.001 mole) of isobutyl chloroformate in dry chloroform was added. The same temperature was maintained for 5-10 minutes, and the temperature was then raised gradually to that of the room (at 0° the sharp odor of  $\alpha$ -toluenethiol appeared). After 20 minutes the solution was evaporated in the air. The oily residue was treated with ether, and the precipitate of triethylamine hydrochloride was filtered off (the yield was quantitative). The ethereal filtrate was evaporated under reduced pressure. The dry residue (0.25 g) smelled strongly of  $\alpha$ -toluenethiol. Recrystallization from aqueous acetone yielded 0.14 g (70%) of 4-isopropylidene-2-phenyl-2-oxazolin-5-one, m.p. 93-96°, undepressed by admixture of 4-isopropylidene-2-phenyl-2-oxazolin-5-one prepared from hippuric acid.

**S,3,3-Trimethyl-N-phenacetyl-L-cysteine.** A solution of 0.42 g (0.003 mole) of methyl iodide in 5 ml of ethanol was added to a solution of 0.96 g (0.003 mole) of S,3,3-dimethyl-N-phenacetyl-L-cysteine in 8 ml of N NaOH (0.003 mole). The ferric chloride reaction for the thiol group disappeared immediately. Alcohol was removed under reduced pressure at room temperature. The alkaline aqueous solution that remained was extracted with ether, acidified to Congo red with concentrated hydrochloric acid, and left in a refrigerator for several hours. The crystalline precipitate was filtered off, washed with water, and dried. The product was 0.6 g (60%) of S,3,3-trimethyl-N-phenacetyl-L-cysteine, m.p. 115-117° (from a 1:3 mixture of benzene and ethyl acetate).

Found %: C 56.82; H 6.52; S 9.59

$C_{16}H_{22}O_4N_2S$ . Calculated %: C 56.80; H 6.50; S 9.46

**4-Isopropylidene-2-(phenylacetamidomethyl)-2-oxazolin-5-one.** A solution of 0.34 g (0.001 mole) of S,3,3-trimethyl-N-phenacetyl-L-cysteine and 0.11 g (0.001 mole) of triethylamine in 5 ml of dry chloroform was cooled to -10°, and a cooled solution of 0.14 g (0.001 mole) of isobutyl chloroformate in dry chloroform was added. After five minutes the temperature was brought to that of the room (the evolution of methanethiol was observed already at 0°) and the reaction mixture was evaporated under reduced pressure. The oily residue solidified when rubbed out with absolute ether. The substance was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.25 g (a quantitative yield) of 4-isopropylidene-2-(phenylacetamidomethyl)-2-oxazolin-5-one, m.p. 121-122° (from absolute alcohol). This oxazolinone is readily soluble in ethyl acetate and alcohol, but insoluble in ether and in water.

Found %: C 65.72; H 6.03; N 10.49

$C_{15}H_{16}O_3N_2$ . Calculated %: C 66.17; H 5.89; N 10.3

#### SUMMARY

1. When treated with chloroformic esters, N-acyl-3,3-dimethyl-L-cysteines give N-acyl-3,3-dimethyl-L-cysteine  $\beta$ -thiolactones in excellent yield. N-Benzoyl-3,3-dimethyl-L-cysteine is an exception, and under the same conditions it loses hydrogen sulfide and is converted into 4-isopropylidene-2-phenyl-2-oxazolin-5-one.
2. When the new thiolactones prepared in this way are treated with aniline, they yield the corresponding N-acyl-3,3-dimethyl-L-cysteine anilides.
3. When N-acyl-S-alkyl (or aralkyl)-3,3-dimethyl-L-cysteines are treated with chloroformic esters, the elimination of thiols readily occurs, and 2-alkyl (or aralkyl)-4-isopropylidene-2-oxazolin-5-ones are formed.

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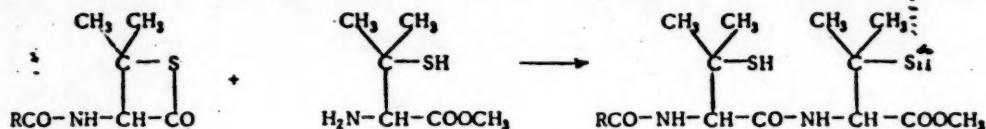


# REACTIONS OF MERCAPTO AMINO ACIDS

## COMMUNICATION 10. NEW METHOD FOR THE SYNTHESIS OF POLYPEPTIDES

I. L. Knunyants, O. V. Kilisheva, and E. Ya. Pervova

We have shown previously [1] that, under the action of dehydrating agents, N-acyl-3,3-dimethylcysteines are readily converted into thiolactones [1]. Further investigation of the properties of the new thiolactones has shown that they are just as reactive as mixed anhydrides of acylamino carboxylic acids, and by their aid we have succeeded in synthesizing di- and tri-peptides of 3,3-dimethylcysteine for the first time. The acylation of 3,3-dimethylcysteine can be carried out with isolated thiolactones, and can be effected also without their isolation in the pure state. In the second case the yield of dipeptide does not exceed 40-50%. By the acylation of the methyl ester of 3,3-dimethylcysteine in ethyl acetate solution at 20° with isolated thiolactones, (N-acetyl-3,3-dimethylcysteinyll- and (3,3-dimethyl-N-phenylacetylcysteinyll)-3,3-dimethylcysteines were prepared in 70-80% yield:

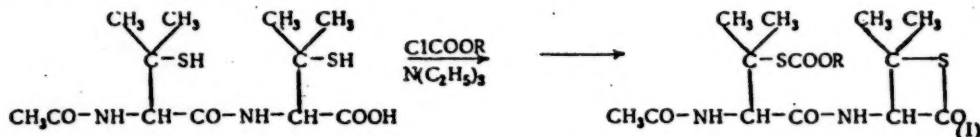


Like the esters of N-acyl-3,3-dimethylcysteine, the esters of N-acylated dipeptides of 3,3-dimethylcysteine do not give the ferric chloride thiol reaction. By hydrolysis with 2 N NaOH at 40-50° they are readily converted into the corresponding dipeptides in 60-70% yield.

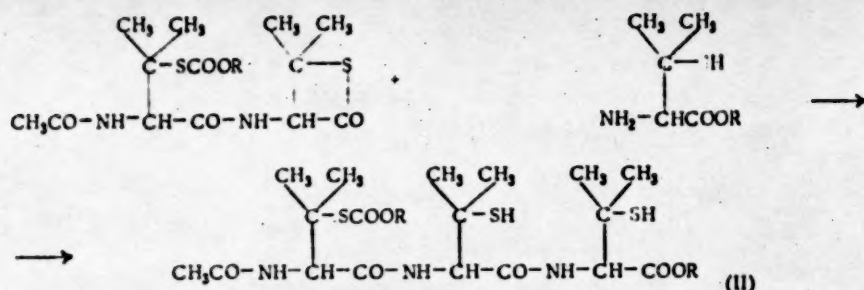
The most convenient method for the preparation of single-component dipeptides was found to be the acylation of 3,3-dimethylcysteine with the isolated thiolactone in an aqueous alkaline medium at 25-35°. Dipeptides were obtained in yields of up to 80-90%. The acylation of various amino acids with thiolactones went just as readily and in excellent yield, and in this way the following mixed dipeptides were isolated: bis(3,3-dimethyl-N-phenylacetylcysteinyll) cysteine, (3,3-dimethyl-N-phenylacetylcysteinyll) valine, and (N-formyl-3,3-dimethylcysteinyll) alanine. The dipeptides obtained were colorless crystalline compounds. The thiol groups of the mixed dipeptides could be detected only by the iodine reaction, owing to the blocking of the carboxyl of the dimethylcysteine. Further investigations showed that dipeptides of 3,3-dimethylcysteine are readily converted into thiolactones, which can then be used in the synthesis of more complex polypeptides.

Thus, by the treatment of (N-acetyl-3,3-dimethylcysteinyll)-3,3-dimethylcysteine with a chloroformic ester in presence of triethylamine in an anhydrous medium, the acylamino thiolactone (I) was obtained.

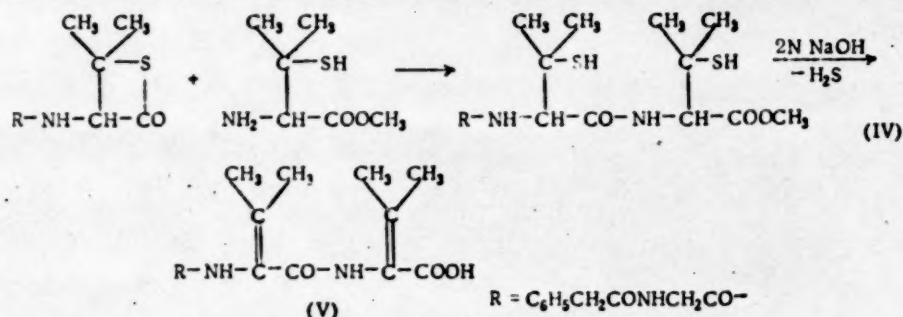
The formation of the substance (I) was generally accompanied by simultaneous acylation of the free thiol group of the 3,3-dimethylcysteinyll residue:



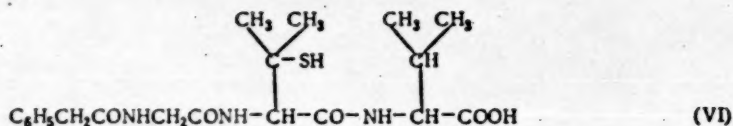
The thiolactone (I) is a stable crystalline compound, which is slowly hydrolyzed by aqueous solutions of caustic alkali. With aniline it readily forms the corresponding anilide, and with the methyl ester of 3,3-dimethylcysteine it forms the tripeptide methyl ester (II):



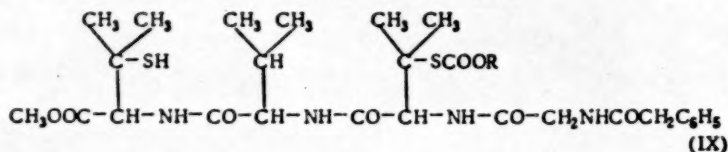
A mixed tripeptide was obtained by the acylation of the methyl ester of 3,3-dimethylcysteine with 3,3-dimethyl-N-phenacetylcysteine  $\beta$ -thiolactone (III) under the same conditions:



Hydrolysis of the tripeptide methyl ester (IV) with alcoholic N NaOH at room temperature gave the tripeptide (3,3-dimethyl-N-phenacetylcysteinyl)-3,3-dimethylcysteine. Hydrolysis of (IV) under more severe conditions (2 N NaOH at 40-50°) was accompanied by the elimination of two molecules of hydrogen sulfide and the formation of 3-methyl-2-(3-methyl-2-phenaceturaminocrotonamido) crotonic acid (V). Acylation of valine with the thiolactone (III) in an aqueous alkaline medium yielded the mixed tripeptide (3,3-dimethyl-N-phenacetylcysteinyl) valine (VI):



The mixed tripeptides were just as readily converted into acylating agents as the dipeptides were. Thus, from the tripeptides (IV) and (VI), the anhydro derivatives (VII) and (VIII), respectively, were prepared, and acylation of the methyl ester of 3,3-dimethylcysteine with (VIII) yielded a mixed tetrapeptide—the methyl ester of [S-(isobutoxycarbonyl)-3,3-dimethyl-N-phenacetylcysteinyl]-valyl-3,3-dimethylcysteine (IX):



There can be no doubt at all that the tetrapeptide (IX) will behave like the di- and tri-peptides of 3,3-dimethylcysteine under similar conditions and will give the corresponding anhydro derivative, by the aid of which it will be possible to obtain a pentapeptide. Our method, therefore, permits the preparation of single-component and mixed polyamides—the latter with a predetermined sequence of amino acids.

#### EXPERIMENTAL

(N-Formyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine. A solution of 0.9 g (0.005 mole) of N-formyl-3,3-dimethylcysteine and 1 g (0.01 mole) of triethylamine in 10 ml of dry chloroform was cooled to -10° and

stirred while addition was made of a cooled solution of 0.65 g (0.005 mole) of isobutyl chloroformate in dry chloroform. The reaction mixture was allowed to stand at  $-6^{\circ}$  until there was no longer a ferric chloride reaction for the thiol group (10 minutes). The mixture was then cooled to  $-10^{\circ}$  and a cooled solution of 0.75 g (0.005 mole) of 3,3-dimethylcysteine in 7.5 ml (0.007 mole) of N NaOH was added. The mixture was stirred vigorously for 15 minutes at  $-5^{\circ}$ , and was then stirred for one hour at room temperature. The aqueous layer was separated, extracted with ether, and acidified to Congo red with 2 N HCl with cooling. The oil that came down slowly solidified. The product was 0.6 g (40%) of (N-formyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine, m.p.  $152-161^{\circ}$ , raised to  $181-183^{\circ}$  by repeated recrystallization from a methanol-ether mixture. The peptide is readily soluble in alcohol and dioxane; it is insoluble in ether, water, and benzene.

Found %: C 43.46; H 6.53; N 8.54; S 19.86

$C_{11}H_{20}O_4N_2S_2$ . Calculated %: C 42.85; H 6.49; N 9.09; S 20.50

Methyl Ester of (N-Acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine. To a solution of 0.5 g (0.0028 mole) of N-acetyl-3,3-dimethylcysteine  $\beta$ -thiolactone [1] in ethyl acetate, 0.45 g (0.0028 mole) of the methyl ester of 3,3-dimethylcysteine was added. The reaction mixture was set aside at room temperature until the next day, when the precipitate formed was filtered off and washed with ethyl acetate. The product was 0.3 g of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine, m.p.  $194-196^{\circ}$  (from ethyl acetate). The ethyl acetate mother liquor was evaporated under reduced pressure, and the oily residue was washed with 2 N HCl and with water; a further 0.4 g of the dipeptide was obtained. The total yield was 0.7 g (73.7%). The methyl ester of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine is readily soluble in alcohol and ethyl acetate, but insoluble in water, ether, and benzene.

Found %: C 46.20; H 7.12; S 19.01; N 8.22

$C_{13}H_{24}O_4N_2S_2$ . Calculated %: C 46.42; H 7.14; S 19.04; N 8.33

(N-Acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine. a) A mixture of 0.5 g (0.0015 mole) of the methyl ester of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine and 2 N NaOH was heated at  $40^{\circ}$  for two hours. The alkaline solution was extracted with ether and then acidified to Congo red with 2 N HCl. The precipitate that formed was filtered off and washed with water. The product was 0.25 g (50%) of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine, melting with decomposition at  $205-206^{\circ}$  (from methanol). (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine is an amorphous substance, readily soluble in alcohol and dioxane, insoluble in water, ether, and benzene. The presence of a thiol group in the dipeptide can be detected by the usual reactions.

Found %: C 44.66; H 7.00; S 19.80; N 8.57

$C_{12}H_{24}O_4N_2S_2$ . Calculated %: C 44.72; H 6.83; S 19.86; N 8.72

Neutralization equivalent: found 316.4; calculated 322

b) A solution of 1.2 g (0.006 mole) of N-acetyl-3,3-dimethylcysteine and 1.2 g (0.012 mole) of triethylamine in 20 ml of dry chloroform was cooled to  $-10^{\circ}$  and stirred while addition was made of a cooled solution of 0.8 g (0.006 mole) of isobutyl chloroformate in dry chloroform. The reaction mixture was allowed to stand at  $-6^{\circ}$  until there was no longer a reaction for thiol with ferric chloride. After 5-10 minutes the solution was cooled to  $-10^{\circ}$  and a cooled solution of 0.9 g (0.006 mole) of 3,3-dimethylcysteine in 6 ml of N NaOH (0.006 mole) was added. The mixture was stirred vigorously at  $0^{\circ}$  for 15 minutes, and was then stirred for one hour at room temperature. The aqueous layer was separated, extracted with ether, cooled, and acidified to Congo red with 2 N HCl. The oil that came down rapidly solidified. It was filtered off and washed with hot water and then methanol. The product was 1.2 g (60%) of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine, melting with decomposition at  $205-206^{\circ}$ . In admixture with the sample prepared in the preceding experiment there was no depression of melting point.

c) To a solution of 0.35 g (0.002 mole) of 3,3-dimethylcysteine in aqueous sodium bicarbonate (0.002 mole), 0.4 g (0.002 mole) of N-acetyl-3,3-dimethylcysteine  $\beta$ -thiolactone [1] was added. The mixture was heated at  $30^{\circ}$  until the thiolactone dissolved and was then left overnight at room temperature. The solution was then extracted several times with ethyl acetate and acidified to Congo red with 25% sulfuric acid; the oil that came down slowly solidified. The precipitate was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.5 g (91% on the amount of thiolactone that reacted) of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine, m.p.  $205-206^{\circ}$ , undepressed by admixture of samples of the dipeptides obtained in the preceding experiments. Evaporation of the ethyl acetate mother liquors resulted in the recovery of 0.1 g of unchanged N-acetyl-3,3-dimethylcysteine  $\beta$ -thiolactone.



Methyl Ester of (3,3-Dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteine. A solution of 0.6 g (0.0024 mole) of 3,3-dimethyl-N-phenylacetylcysteine  $\beta$ -thiolactone and 0.4 g (0.0024 mole) of the methyl ester of 3,3-dimethylcysteine was prepared in ethyl acetate and was then left at room temperature overnight. The crystalline precipitate that formed was filtered off, washed with ethyl acetate, and dried. The product was 0.55 g of the methyl ester of (3,3-dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteine. The ethyl acetate mother liquor yielded a further 0.25 g of the dipeptide, the total yield being 80%. After recrystallization from absolute ethanol the melting point was 155-161°. The dipeptide is a colorless crystalline substance, readily soluble in alcohol and ethyl acetate, but insoluble in water and ether. The presence of a thiol group can be detected with iodine.

Found %: C 55.30; H 6.90; S 15.68; N 6.92  
 $C_{19}H_{21}O_4N_2S_2$ . Calculated %: C 55.33; H 6.79; S 15.53; N 6.79

(3,3-Dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteine. The methyl ester of (3,3-dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteine (0.4 g, 0.001 mole) was heated with 2 N NaOH at 40-50° for two hours. The solution was filtered, extracted with ether, cooled, and acidified with 25% sulfuric acid. The oil that separated rapidly solidified. The precipitate was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator; it was then again washed with ether and dried. The product was 0.3 g (77%) of (3,3-dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteine, melting with decomposition at 178-182° (from absolute alcohol).

(3,3-Dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteine is readily soluble in alcohol, chloroform, and dioxane, but insoluble in water and ether. The presence of the thiol group can be detected both with iodine and with ferric chloride.

Found %: C 54.08; H 6.93; S 15.23; N 6.78  
 $C_{18}H_{20}O_4N_2S_2$ . Calculated %: C 54.27; H 6.53; S 16.03; N 7.03

Bis(3,3-Dimethyl-N-phenylacetylcysteinyl)cystine. To a solution of 0.12 g (0.0005 mole) of cystine in 1 ml of N NaOH (0.001 mole), 0.25 g (0.001 mole) of 3,3-dimethyl-N-phenylacetylcysteine  $\beta$ -thiolactone was added. The mixture was heated to 50° and then left at room temperature overnight. On the next day the solution was extracted with ethyl acetate and acidified to Congo red with 2 N HCl with cooling. The amorphous precipitate that formed was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.35 g of bis(3,3-dimethyl-N-phenylacetylcysteinyl)cystine, which had a decomposition temperature of 96°. The substance was purified by precipitation from methanol solution with absolute ether (repeated twice), and it then melted with decomposition at 160°. The dipeptide is readily soluble in alcohol, but insoluble in water, ether, and benzene. The presence of the thiol group could be detected only by the iodine reaction.

Found %: S 16.15; N 7.39  
 $C_{32}H_{40}O_8N_4S_4$ . Calculated %: S 17.34; N 7.58

(3,3-Dimethyl-N-phenylacetylcysteinyl)valine. Valine (0.12 g, i.e. 0.001 mole) was dissolved in an aqueous solution of sodium bicarbonate (0.001 mole), and 0.25 g (0.001 mole) of 3,3-dimethyl-N-phenylacetylcysteine  $\beta$ -thiolactone was added. The mixture was heated in a water bath at 40-45° until the thiolactone dissolved (20 minutes), and was then left overnight. It was then filtered, and the filtrate was extracted with ethyl acetate and acidified to Congo red with sulfuric acid with cooling. The oil that separated solidified after some time. The product was 0.3 g of (3,3-dimethyl-N-phenylacetylcysteinyl)valine, decomposition temperature 159°, raised to 183° by two crystallizations from absolute ethanol. The dipeptide is readily soluble in alcohol, dioxane, ethyl acetate, and chloroform, but insoluble in water and ether. The presence of a thiol group can be detected only by the iodine reaction.

Found %: C 58.71; H 6.96; S 8.72; N 7.67  
 $C_{18}H_{26}O_4N_2S$ . Calculated %: C 59.01; H 7.10; S 8.74; N 7.65

(N-Formyl-3,3-dimethylcysteinyl)alanine. To a solution of 0.18 g (0.002 mole) of alanine in 2 ml of N NaOH (0.002 mole), 0.32 g (0.002 mole) of N-formyl-3,3-dimethylcysteine  $\beta$ -thiolactone was added. The mixture was heated at 40° for 20 minutes and then set aside at room temperature overnight. The solution was extracted with ethyl acetate, acidified with 2 N HCl with cooling, and evaporated under reduced pressure until crystallization set in. The product was 0.35 g of (N-formyl-3,3-dimethylcysteinyl)alanine, decomposition temperature 163°. The mother liquor yielded a further 0.1 g of the dipeptide, the total yield being 0.45 g. After recrystallization from ethanol the decomposition temperature was 163°. The dipeptide is readily soluble in alcohol, dioxane, and water, but insoluble in ether, ethyl acetate and benzene. The presence of a thiol group can be detected by the iodine reaction.



Found %: C 43.94; H 6.49; S 13.28; N 10.90  
 $C_9H_{16}O_4N_2S$ . Calculated %: C 43.58; H 6.45; S 12.90; N 11.29

[N-Acetyl-S-(isobutoxycarbonyl)-3,3-dimethylcysteinyl]-3,3-dimethylcysteine  $\beta$ -Thiolactone (I). A solution of 0.30 g (0.001 mole) of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine and 0.3 g (0.003 mole) of triethylamine in dry chloroform was cooled to  $-10^\circ$ , and at this temperature a solution of 0.14 g (0.001 mole) of isobutyl chloroformate in dry chloroform was added. Five minutes after a ferric chloride reaction ceased to be obtained for the thiol group, the temperature was gradually raised to that of the room. Solvent was removed under reduced pressure. The oily residue was rubbed out with ether, and the precipitate then formed was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.1 g of the thiolactone (I), m.p. 196-198° (from absolute alcohol). The thiolactone does not react with water at room temperature, but when heated with water it is readily hydrolyzed with formation of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine. It is readily soluble in alcohol, chloroform, and ethyl acetate, but insoluble in water and ether.

Found %: C 50.16; H 6.92; S 15.80; N 6.77  
 $C_{17}H_{28}O_5N_2S_2$ . Calculated %: C 50.49; H 6.93; S 15.84; N 6.93

Anilide of [N-Acetyl-S-(isobutoxycarbonyl)-3,3-dimethylcysteinyl]-3,3-dimethylcysteine. A solution of 0.1 g (0.0002 mole) of the thiolactone (I) and 0.04 g (0.0004 mole) of aniline was prepared in ethyl acetate as solvent and was set aside at room temperature overnight. The crystalline precipitate formed was then filtered off, washed with 2 N HCl and then water, and dried. The product was 0.1 g of the anilide of [N-acetyl-S-(isobutoxycarbonyl)-3,3-dimethylcysteinyl]-3,3-dimethylcysteine, m.p. 226-229° (from absolute alcohol). The anilide is readily soluble in alcohol, but insoluble in water, ethyl acetate, and ether.

Found %: C 55.08; H 7.05; S 13.09; N 8.76  
 $C_{23}H_{25}O_5N_3S_2$ . Calculated %: C 55.53; H 7.04; S 12.88; N 8.45

Methyl Ester of [N-Acetyl-S-(isobutoxycarbonyl)-3,3-dimethylcysteinyl]-3,3-dimethylcysteine (II). A solution of 0.1 g (0.00025 mole) of [N-acetyl-S-(isobutoxycarbonyl)-3,3-dimethylcysteinyl]-3,3-dimethylcysteine  $\beta$ -thiolactone and 0.04 g (0.00025 mole) of the methyl ester of 3,3-dimethylcysteine was prepared in ethyl acetate as solvent and was set aside at room temperature overnight. The precipitate formed was filtered off, washed with ether, and dried. The product was 0.1 g of the methyl ester of [N-acetyl-S-(isobutoxycarbonyl)-3,3-dimethylcysteinyl]-3,3-dimethylcysteine, melting with decomposition at 236-238° (from absolute alcohol). The dimethylcysteine tripeptide (II) is an amorphous substance, readily soluble in alcohol, but insoluble in water, ether, and ethyl acetate.

Found %: C 48.00; H 7.10; S 16.85; N 7.36  
 $C_{23}H_{41}O_7N_3S_3$ . Calculated %: C 48.67; H 7.31; S 16.94; N 7.38

Methyl Ester of (3,3-Dimethyl-N-phenacetylrcysteinyl)-3,3-dimethylcysteine (IV). 3,3-Dimethyl-N-phenacetylrcysteine  $\beta$ -thiolactone (III) [1] (0.2 g, i.e. 0.00065 mole) and the methyl ester of 3,3-dimethylcysteine (0.1 g, i.e. 0.00065 mole) was heated with 20 ml of absolute methanol until a solution was obtained. The solution was set aside at room temperature overnight. Solvent was removed under reduced pressure, and the oily residue was rubbed out with ether. The precipitate formed was filtered off and washed with hot ethyl acetate. The product was 0.21 g of the methyl ester of (3,3-dimethyl-N-phenacetylrcysteinyl)-3,3-dimethylcysteine, m.p. 192-200°. The tripeptide (IV) is soluble in alcohol and ethyl acetate, but insoluble in water, ether, and chloroform. In this tripeptide the thiol group can be detected only by the iodine reaction.

Found %: C 53.33; H 6.47; S 13.15; N 8.29  
 $C_{21}H_{30}O_5N_3S_2$ . Calculated %: C 53.84; H 6.41; S 13.67; N 8.91.

(3,3-Dimethyl-N-phenacetylrcysteinyl)-3,3-dimethylcysteine. a) Hydrolysis of (IV) with alcoholic NaOH. The methyl ester of (3,3-dimethyl-N-phenacetylrcysteinyl)-3,3-dimethylcysteine (0.25 g, i.e. 0.0005 mole) was dissolved in excess of alcoholic N NaOH, and the solution was set aside at room temperature overnight. Solvent was removed under reduced pressure, and the residue was dissolved in water. The solution was acidified to Congo red with 2 N HCl, and an oil formed, which solidified when the mixture was placed in a refrigerator. The precipitate was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.15 g (68%) of (3,3-dimethyl-N-phenacetylrcysteinyl)-3,3-dimethylcysteine, melting with decomposition at 199-203° (from a mixture of ethyl acetate and methanol). (3,3-Dimethyl-N-phenacetylrcysteinyl)-3,3-dimethylcysteine is readily soluble in water and ether.

Found %: S 13.39; N 8.77  
 $C_{20}H_{28}O_5N_2S_2$ . Calculated %: S 14.06; N 9.23

b) 3,3-Dimethyl-N-phenacetyl-L-cysteine  $\beta$ -thiolactone (1 g, i.e. 0.003 mole) was added to a solution of 0.5 g (0.003 mole) of 3,3-dimethyl-L-cysteine in aqueous sodium bicarbonate (0.003 mole). The mixture was heated at 30° until the thiolactone was dissolved, and was then set aside at room temperature overnight. On the next day the solution was extracted with ethyl acetate and acidified to Congo red with 25% sulfuric acid. When the mixture was cooled, the precipitated oil solidified. It was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.9 g (60%) of (3,3-dimethyl-N-phenacetyl-L-cysteinyl)-3,3-dimethyl-L-cysteine, m.p. 155-168°, raised by repeated recrystallizations from dioxane and alcohol to 199-203°. In admixture with the product of the preceding experiment there was no depression in melting point.

3-Methyl-2-(3-methyl-2-phenacetamidocrotonamido)crotonic Acid (V). The methyl ester of (3,3-dimethyl-N-phenacetyl-L-cysteinyl)-3,3-dimethyl-L-cysteine (0.46 g, i.e. 0.001 mole) was heated for two hours at 50-60° with 2 N NaOH. The solution was cooled, extracted with ether, and acidified to Congo red with 2 N HCl. The only precipitate formed solidified after a time and was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.25 g (65%) of 3-methyl-2-(3-methyl-2-phenacetamidocrotonamido)crotonic acid, m.p. 193-196° (from ethanol). The acid (V) decolorizes a solution of bromine in chloroform, and it is readily soluble in alcohol and dioxane, poorly soluble in ethyl acetate and acetone, and insoluble in ether and water.

Found %: C 61.50; H 6.41; N 10.08  
 $C_{20}H_{25}O_5N_3$ . Calculated %: C 62.00; H 6.45; N 10.85

(3,3-Dimethyl-N-phenacetyl-L-cysteinyl)valine (VI). 3,3-Dimethyl-N-phenacetyl-L-cysteine  $\beta$ -thiolactone (0.15 g) was dissolved in warm alcohol, an aqueous solution of the sodium salt prepared from 0.66 g of valine was added, and the mixture was heated to 50°. On the next day the mixture was evaporated under reduced pressure to one-third bulk and was then acidified to Congo red with 2 N HCl. The precipitate formed was filtered off, washed with water, and dried. The product was 0.15 g of (3,3-dimethyl-N-phenacetyl-L-cysteinyl)valine, melting with decomposition at 178-184° (from absolute ethanol).

Found %: C 56.85; H 6.93; S 7.36; N 10.1  
 $C_{20}H_{29}O_5N_3S$ . Calculated %: C 56.73; H 6.85; S 7.54; N 9.92

[S-(Isobutoxycarbonyl)-3,3-dimethyl-N-phenacetyl-L-cysteinyl]-3,3-dimethyl-L-cysteine  $\beta$ -Thiolactone (VII). A solution of 0.2 g (0.0004 mole) of (3,3-dimethyl-N-phenacetyl-L-cysteinyl)-3,3-dimethyl-L-cysteine and 0.13 g (0.0012 mole) of triethylamine in dry chloroform was cooled to -10°, and at this temperature a solution of 0.084 g (0.0006 mole) of isobutyl chloroformate in dry chloroform was added. Five minutes after the ferric chloride reaction for thiol ceased to be obtained, the temperature was brought to that of the room. Solvent was removed under reduced pressure, the residue was rubbed out with ether, and the precipitate was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.14 g of the thiolactone (VII), m.p. 130-141°, raised to 164-166° (with decomposition) by recrystallization from aqueous acetone. The thiolactone gradually decolorized iodine. After hydrolysis with alcoholic caustic alkali at room temperature, a positive reaction for the thiol group was given.

Found %: C 55.01; H 6.67; S 11.48; N 7.86  
 $C_{25}H_{35}O_6N_3S_2$ . Calculated %: C 55.86; H 6.70; S 11.91; N 7.82

Conversion of (3,3-Dimethyl-N-phenacetyl-L-cysteinyl)valine into the Anhydride (VIII). A solution of 0.43 g (0.001 mole) of (3,3-dimethyl-N-phenacetyl-L-cysteinyl)valine (VI) and 0.2 g (0.002 mole) of triethylamine in dry chloroform was cooled to -10°, and at this temperature a solution of 0.28 g (0.002 mole) of isobutyl chloroformate in dry chloroform was added. After 10 minutes the temperature was brought to that of the room. Solvent was removed under reduced pressure and the residue was rubbed out with ether. Triethylamine hydrochloride was filtered off. The product was 0.25 g of the substance (VIII), melting with decomposition at 155-158°. The substance (VIII) is readily soluble in alcohol and dioxane, poorly soluble in ether, and insoluble in water.

Found %: C 58.91; H 6.82; S 6.14; N 8.57  
 $C_{25}H_{36}O_6N_3S$ . Calculated %: C 59.40; H 6.93; S 6.33; N 8.31

Methyl Ester of [S-(Isobutoxycarbonyl)-3,3-dimethyl-N-phenacetyl-L-cysteinyl]-valyl-3,3-dimethyl-L-cysteine (IX). A solution of 0.1 g (0.0002 mole) of the substance (VIII) and 0.04 g (0.00025 mole) of the

methyl ester of 3,3-dimethylcysteine was prepared in ethyl acetate as solvent and was set aside at room temperature overnight. The solution was filtered, and was washed with 2 N HCl, with water, with sodium bicarbonate solution, and again with water. It was dried over magnesium sulfate, and solvent was removed under reduced pressure. The residue was reprecipitated three times from ethyl acetate solution by means of ether; it then melted with decomposition at 145-178°. The tetrapeptide (IX) is an amorphous substance, and could not be crystallized. The presence of the thiol group can be detected only by the iodine reaction; with ferric chloride the reaction is negative.

Found %: C 56.19; H 7.06; N 7.84  
C<sub>31</sub>H<sub>48</sub>O<sub>8</sub>N<sub>4</sub>S<sub>2</sub>. Calculated %: C 55.63; H 7.18; N 8.38

#### SUMMARY

1. It was shown that N-acyl-3,3-dimethylcysteine 2-thiolactones are active acylating agents, similar in properties to mixed anhydrides. By the acylation of amino acids with these 3-thiolactones, various polyamides can be prepared, and these include compounds containing residues of mercapto amino acids. A fundamentally new method for the synthesis of polypeptides has therefore been provided.

2. By the aid of the new method, di- and tri-peptides were prepared, and these include both polypeptides derived entirely from mercapto amino acids and also mixed polypeptides.

#### LITERATURE CITED

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\* T. p. = C. B. Translation pagination

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# ADDITION REACTIONS OF PERFLUOROOLEFINS

## COMMUNICATION 3. ADDITION OF SULFUR CHLORIDES

I. L. Knunyants and A. V. Fokin

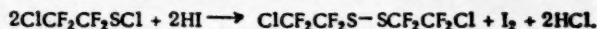
It has been shown in previous communications [1, 2] that perfluoroolefins are peculiar chemically in their ability to undergo ready addition with nucleophilic reagents (alkoxides, thiols, amines, etc.). It was then suggested that the primary process determining addition to perfluoroolefins is the anionoid attack of the nucleophilic reagent resulting from electron deficiency in the  $\pi$ -bond of the perfluoroolefin. The  $\pi$ -bond of the tetrafluoroethylene molecule plays the part of an electron-acceptor in reactions with nucleophilic reagents, whereas in the usual olefins it acts as an electron-donor. The peculiar structure of the  $\pi$ -bond of perfluoroolefins explains also the difficulty with which electrophilic reagents add to them.

After many unsuccessful attempts, in 1950 we succeeded in bringing about the addition of sulfur chlorides to tetrafluoroethylene. It was found that this reaction, unlike that of the usual olefins with sulfur chlorides (which go readily in the cold), takes place only at high temperature and under pressure. When tetrafluoroethylene was heated with sulfur monochloride at 80-90° for 6-8 hours, only a low yield (not more than 18-20%) of addition products was obtained. Only when the mixture was heated at 100-120° for six hours was it found possible to attain a yield of about 80%. The product of the reaction of tetrafluoroethylene with sulfur monochloride was a complex mixture, consisting of mono-, di-, tri-, and poly-sulfides and various sulfenyl chlorides. By fractionation the following previously unknown compounds were isolated: 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride (I), bis(2-chloro-1,1,2,2-tetrafluoroethyl) sulfide (IV), bis(2-chloro-1,1,2,2-tetrafluoroethyl)disulfide (V), and higher polysulfides (see table).

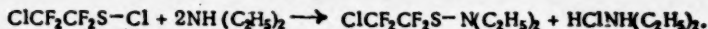
The main reaction product was bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide. Purification of this disulfide presented much difficulty, and even after many distillations it could not be freed from material containing active chlorine. When the crude disulfide was boiled with cyclohexene, subsequent fractional distillation yielded the disulfide in a pure state, and it was shown that the impurity originally present in the disulfide was 1-chloro-2-(chlorodithio)-1,1,2,2-tetrafluoroethane (II), which reacts with cyclohexene with formation of the high-boiling 2-chlorocyclohexyl 2-chloro-1,1,2,2-tetrafluoroethyl disulfide (IX), readily separable from bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide by distillation. The latter compound, therefore, was obtained in the pure state. The structure of bis(2-chloro-1,1,2,2-tetrafluoroethyl)disulfide was proved by the chlorine cleavage reaction. This reaction, which proceeds with most aliphatic disulfides with evolution of heat, was here found to require unexpectedly severe conditions. Negative results were obtained when dry chlorine was passed for two hours at room temperature and when treatments were given in a sealed tube with sulfuryl chloride at 120-140° and with bromine at 120°. It was found possible to effect the cleavage of the disulfide in quantitative yield by the action of chlorine at 80-90° (in an autoclave):



The reaction product was a clear, mobile liquid, b.p. 69.5°. Analysis for active chlorine, fluorine, and sulfur showed that the compound was 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride. It liberated iodine from potassium iodide solution, and by treatment of an ethereal solution of the sulfenyl chloride with potassium iodide solution, a satisfactory yield of the original bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide was obtained:



2-Chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride reacted smoothly with diethylamine with formation of N,N-diethyl-2-chloro-1,1,2,2-tetrafluoroethanesulfenamide (III):



It was found, however, that 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride is less reactive toward olefins than its hydrogen analog. At ordinary temperatures it adds neither to ethylene nor to cyclohexene. The sulfides formed with ethylene and with cyclohexene were obtained only when the reactants were heated in a sealed glass

tube. The products were 2-chloroethyl 2-chloro-1,1,2,2-tetrafluoroethyl sulfide (VII) and 2-chlorocyclohexyl 2-chloro-1,1,2,2-tetrafluoroethyl sulfide (VIII).

The addition of sulfur dichloride to tetrafluoroethylene was carried out at 100-110°, and the yield of addition products attained 80%. The products were the same as those of the reaction with sulfur monosulfide. The chlorine formed by the dissociation of sulfur dichloride reacted with tetrafluoroethylene and with the addition products, and the reaction mixture was enriched in sulfenyl chlorides formed by the cleavage of di- and poly-sulfides. The amount of disulfide was therefore correspondingly reduced, and it was found to be possible to isolate 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride and 1-chloro-2-(chlorodithio)-1,1,2,2-tetrafluoroethane in appreciable amounts. When the chlorodithio compound, which was isolated in the pure state, was heated with cyclohexene, it was converted in good yield into 2-chlorocyclohexyl 2-chloro-1,1,2,2-tetrafluoroethyl disulfide, which was isolated previously from the products of the treatment of a reaction mixture with cyclohexene. The di- and tri-sulfides obtained were found to be stable substances.

TABLE

Formula	B.p. in °C (p in mm)	Sp. gr. at 20°	Refractive index at 20°
$\text{ClCF}_2\text{CF}_2\text{SCl}$ (I)	69.5°	1.605	1.3890
$\text{ClCF}_2\text{CF}_2\text{S}-\text{SCl}$ (II)	126	1.674	1.4112
$\text{ClCF}_2\text{CF}_2\text{S}-\text{N}(\text{C}_2\text{H}_5)_2$ (III)	66-67 (60)	1.341	1.4850
$\text{ClCF}_2\text{CF}_2\text{SCF}_2\text{CF}_2\text{Cl}$ (IV)	100-102	1.662/10°	1.368/10°
$\text{ClCF}_2\text{CF}_2\text{S}-\text{SCF}_2\text{CF}_2\text{Cl}$ (V)	139-140	1.685	1.3970
$\text{ClCF}_2\text{CF}_2\text{S}-\text{S}-\text{SCF}_2\text{CF}_2\text{Cl}$ (VI)	50-52 (5)	1.707	1.4340
$\text{ClCF}_2\text{CF}_2-\text{S}-\text{CH}_2\text{CH}_2\text{Cl}$ (VII)	85 (100)	1.528	1.4218
$\text{ClCF}_2\text{CF}_2-\text{S}-\text{CH}-\text{CHCl}$ (VIII)	135-136 (60)	1.388	1.4595
<div><div><div><div><div><math>\text{CH}_2</math></div><div><math>\text{CH}_2</math></div></div><div><div><math>\text{CH}_2-\text{CH}_2</math></div></div></div></div><div><math>\text{ClCF}_2\text{CF}_2-\text{S}-\text{S}-\text{CH}-\text{CHCl}</math> (IX)</div></div>	142 (20)	1.456	1.4915

Fraction IV, b.p. 50-52° (5 mm); 3 g

Fraction V, b.p. 96-98° (5 mm); 2 g

Redistillation of Fraction I yielded about 2 g of a substance boiling at 69-70°. This was 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride and had  $d_4^{20}$  1.604;  $n_D^{20}$  1.3893; found MR 29.93; calculated MR 29.49.

Found %: S 15.44; F 34.22

$\text{C}_2\text{SF}_4\text{Cl}_2$ . Calculated %: S 15.80; F 34.70

Fraction II yielded a substance boiling at 100-102°. This was bis(2-chloro-1,1,2,2-tetrafluoroethyl) sulfide;  $d_4^{10}$  1.662;  $n_D^{10}$  1.368; found MR 40.06; calculated MR 39.16.

Found %: S 11.02; Cl 22.75; F 47.55

$\text{C}_4\text{F}_8\text{Cl}_2\text{S}$ . Calculated %: S 11.50; Cl 23.40; F 49.90

Fraction III was purified by heating it with cyclohexene and then distilling at ordinary pressure, when bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide was isolated in 35% yield (11.7 g). It is a colorless, mobile liquid, b.p. 139-140°;  $d_4^{20}$  1.685;  $n_D^{20}$  1.3970; found MR 47.60; calculated MR 46.85.

Found %: S 18.72; F 45.37; Cl 21.17

$\text{C}_4\text{F}_8\text{Cl}_2\text{S}_2$ . Calculated %: S 19.10; F 45.45; Cl 21.22

Found M 332.6 (cryoscopically)

Calculated M 335

## EXPERIMENTAL

1. Products of the Addition of Sulfur Monochloride to Tetrafluoroethylene. A mixture of 13.5 g of freshly distilled sulfur monochloride and 25 g of liquid tetrafluoroethylene was prepared in a stainless steel cylinder, which was hermetically sealed and then heated with constant agitation at 100-120° for six hours. Unchanged tetrafluoroethylene (1.5 liters) was driven off, and 28 g of addition products was obtained. The reaction mixture - a clear, light-yellow liquid - was fractionated at ordinary pressure, and yielded:

Fraction I, b.p. 68-74°, 2.8 g

Fraction II, b.p. 95-105°, 3.5 g

Fraction III, b.p. 130-142°, 1.4 g

The residue was fractionated at reduced pressure and yielded:

Vacuum distillation of Fraction IV yielded bis(2-chloro-1,1,2,2-tetrafluoroethyl) trisulfide, a colorless oily liquid, b.p. 50–52° (5mm);  $d_4^{20}$  1.707;  $n_D^{20}$  1.4340; found MR 55.60; calculated MR 54.52.

Found %: S 25.84; Cl 19.94; F 41.42

$C_4S_3F_8Cl_2$ . Calculated %: S 26.16; Cl 19.34; F 41.25

The fractions of still higher boiling point were not investigated.

**2. 2-Chloro-1,1,2,2-tetrafluoroethanesulfonyl Chloride.** A mixture of 12 g of bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide and 5 g of dry liquid chlorine was prepared in a stainless steel cylinder, which was hermetically sealed and heated with agitation at 95–100° for two hours. The residue after removal of excess of chlorine was 15 g of a light-yellow liquid, which had the characteristic odor of sulfonyl chlorides. Fractionation yielded 13 g of a substance boiling at 69.5°. This was 2-chloro-1,1,2,2-tetrafluoroethanesulfonyl chloride, obtained in 89% yield. It is a light-yellow mobile liquid, for which  $d_4^{20}$  1.605;  $n_D^{20}$  1.3890; found MR 30.04; calculated MR 29.49.

Found %: S 15.82; Cl 34.80; F 37.11

$C_2SF_4Cl_2$ . Calculated %: S 15.80; Cl 34.70; F 37.42

**3. 2-Chloroethyl 2-Chloro-1,1,2,2-tetrafluoroethyl Sulfide.** A solution of 25 g of 2-chloro-1,1,2,2-tetrafluoroethanesulfonyl chloride in 40 g of carbon tetrachloride was introduced into a 250-ml stainless steel autoclave, which was then filled with ethylene from a cylinder until the pressure attained 35 atm. The autoclave was heated with continuous rotation for three hours at 95–100°, and the pressure in the autoclave fell to 19 atm. Excess of ethylene was removed from the reaction mixture, and the solvent was distilled off. The liquid residue (9 g) was vacuum-fractionated, and it yielded a main fraction boiling at 82–86° (100 mm). Redistillation yielded pure 2-chloroethyl-2-chloro-1,1,2,2-tetrafluoroethyl sulfide, a clear colorless oil liquid of characteristic odor and having b. p. 85° (100 mm);  $d_4^{20}$  1.528;  $n_D^{20}$  1.4218; found MR 38.39; calculated MR 38.72.

Found %: S 13.14; Cl 29.35; F 32.32

$C_4H_4F_7Cl_2S$ . Calculated %: S 13.85; Cl 30.73; F 32.90

**4. 2-Chlorocyclohexyl 2-Chloro-1,1,2,2-tetrafluoroethyl Sulfide.** A mixture of 3 g of 2-chloro-1,1,2,2-tetrafluoroethanesulfonyl chloride and 4 g of cyclohexene was sealed in a tube, which was then heated in a water bath for one hour at 60–80°. Excess of cyclohexene was distilled off, and the residue (about 4.5 g) was vacuum-fractionated. The main fraction was collected at 135–136° (60 mm). Redistillation under vacuum yielded pure 2-chlorocyclohexyl 2-chloro-1,1,2,2-tetrafluoroethyl sulfide, a clear colorless oily liquid having b.p. 135° (60 mm);  $d_4^{20}$  1.388;  $n_D^{20}$  1.4595; found MR 56.15; calculated MR 55.00.

Found %: S 11.55; Cl 24.52; F 28.15

$C_8H_{10}F_4SCl_2$ . Calculated %: S 11.23; Cl 24.91; F 26.66

**5. 2-Chlorocyclohexyl 2-Chloro-1,1,2,2-tetrafluoroethyl Disulfide.** The residue that remained after the distillation at ordinary pressure of the oil obtained by the treatment of crude bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide with cyclohexene (Experiment 1) was vacuum-distilled and yielded a substance boiling at 142° (20 mm). This was 2-chlorocyclohexyl 2-chloro-1,1,2,2-tetrafluoroethyl disulfide, having  $d_4^{20}$  1.456 and  $n_D^{20}$  1.4915.

Found %: S 20.04; Cl 21.25; F 24.53

$C_8H_{10}F_4Cl_2$ . Calculated %: S 29.40; Cl 22.40; F 23.96

A mixture of this disulfide (4.6 g) and dry liquid chlorine (3 g) was prepared in a 30-ml steel cylinder, which was hermetically sealed and heated at 100° for two hours. The residue remaining after removal of excess of chlorine was about 6 g of a liquid having an odor of sulfonyl chlorides. Fractionation yielded 3 g of a substance boiling at 69–70°. It was a clear mobile light-yellow liquid having  $d_4^{20}$  1.605 and  $n_D^{20}$  1.3899 (2-chloro-1,1,2,2-tetrafluoroethanesulfonyl chloride).

Found %: S 15.38; Cl 34.33; F 36.85

$C_2SF_4Cl_2$ . Calculated %: S 15.80; Cl 34.70; F 37.42

**6. Products of the Addition of Sulfur Dichloride to Tetrafluoroethylene.** A mixture of 10.3 g of freshly prepared sulfur dichloride and 24 g of liquid tetrafluoroethylene was prepared in a 100-ml stainless steel cylinder, which was hermetically sealed and heated at 100–110° for five hours. The cylinder was cooled, and the excess of tetrafluoroethylene was driven off (0.8 liter). The weight of the liquid residue was 25.5 g. Fractionation yielded:



Fraction I	B.p. 66-70°; 6 g
Fraction II	B.p. 120-128°; 8.5 g
Fraction III	B.p. 126-142°; 3 g

The residue remaining undistilled at ordinary pressure was 4.5 g.

Redistillation of Fraction I yielded 2-chloro-1,1,2,2-tetrafluoroethanesulfonyl chloride, b.p. 69-70°;  $d_4^{20}$  1.681;  $n_D^{20}$  1.3955.

Fraction II yielded 1-chloro-2-(chlorodithio)-1,1,2,2-tetrafluoroethane, a mobile orange liquid having b.p. 126°;  $d_4^{20}$  1.674;  $n_D^{20}$  1.4112.

Found %: S 27.38; Cl 30.82; F 33.11  
 $C_2F_4Cl_2S_2$ . Calculated %: S 27.20; Cl 30.25; F 32.35

7. Addition of Cyclohexene to 1-Chloro-2-(chlorodithio)-1,1,2,2-tetrafluoroethane. A mixture of 8 g of 1-chloro-2-(chlorodithio)-1,1,2,2-tetrafluoroethane and 4 g of cyclohexene was sealed in a glass tube, which was then heated at 60° for two hours. Fractionation of the reaction mixture yielded a substance having b.p. 136-137° (18 mm),  $d_4^{20}$  1.458, and  $n_D^{20}$  1.4912 (2-chlorocyclohexyl 2-chloro-1,1,2,2-tetrafluoroethyl disulfide).

Found %: S 20.83; Cl 20.10; F 23.22  
 $C_8H_{10}S_2F_4Cl_2$ . Calculated %: S 20.19; Cl 22.40; F 23.96

8. Bis(2-chloro-1,1,2,2-tetrafluoroethyl) Disulfide. A solution of 12 g of 2-chloro-1,1,2,2-tetrafluoroethanesulfonyl chloride in 100 ml of ether was introduced into a 250-ml separating funnel, and 10% potassium iodide solution was added gradually, the reaction mixture being carefully shaken after each addition. The ether layer was separated, washed with thiosulfate solution, and dried with calcined magnesium sulfate. After removal of ether, the residue was fractionated at ordinary pressure. The main fraction boiled at 133-144°. Redistillation yielded a substance boiling at 140-141° (4.5 g), which corresponded in physical properties to bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide. It had  $d_4^{20}$  1.685 and  $n_D^{20}$  1.3965.

Found %: S 19.87  
 $C_4F_8Cl_2S_2$ . Calculated %: S 19.10

9. N,N-Diethyl-2-chloro-1,1,2,2-tetrafluoroethanesulfenamide. A solution of 8 g of 2-chloro-1,1,2,2-tetrafluoroethanesulfonyl chloride in 50 ml of dry ether was introduced into a 100-ml round-bottomed flask fitted with a stirrer. The solution was constantly stirred and cooled while a solution of 4 g of diethylamine in dry ether was added in small portions. Reaction was accompanied by the evolution of much heat. The solution was separated from the precipitate of diethylamine hydrochloride, and ether was then distilled off. Vacuum fractionation yielded a main fraction boiling at 64-69° (60 mm), and redistillation gave pure N,N-diethyl-2-chloro-1,1,2,2-tetrafluoroethanesulfenamide, b.p. 66-67° (60 mm),  $d_4^{20}$  1.341 and  $n_D^{20}$  1.4850.

Found %: S 12.94; N 6.21; F 32.54  
 $C_6H_{10}F_4ClSN$ . Calculated %: S 13.20; N 5.86; F 31.75

#### SUMMARY

1. Reaction of sulfur chlorides with tetrafluoroethylene yielded bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide, 2-chloro-1,1,2,2-tetrafluoroethanesulfonyl chloride, and 1-chloro-2-(chlorodithio)-1,1,2,2-tetrafluoroethane. When treated with chlorine, bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide was converted into 2-chloro-1,1,2,2-tetrafluoroethanesulfonyl chloride.

2. Unlike its hydrogen analog, 2-chloro-1,1,2,2-tetrafluoroethanesulfonyl chloride adds to olefins only under severe conditions. By the reaction of this sulfonyl chloride with ethylene and with cyclohexene, the corresponding sulfides were prepared.

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\* T.p. = C. B. Translation pagination.

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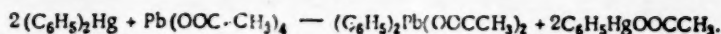
# DEARYLATION OF $Ar_2PbX_2$ AS A METHOD OF SYNTHESIZING

## A NEW CLASS OF COMPOUNDS $ArPbX_3$

K. A. Kocheshkov and E. M. Panov

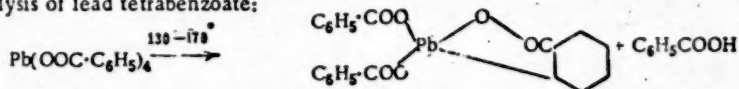
Of the existing three classes of organolead compounds  $R_3PbX$ ,  $R_2PbX_2$ , and  $RPbX_3$  (X is an acid residue and R an aliphatic or aromatic radical) the first two have been studied for a long time. Prior to our investigations [1, 2] no compounds of the last type containing aromatic radicals were known, and although compounds of formula  $RPbX_3$  containing aliphatic radicals have been described, the available data on these is, for various reasons (see below), in need of verification.

In approaching the problem of synthesizing  $ArPbX_3$  we may make use of analogies to other organometallic compounds of Group IV of the periodic system, taking into account, however, the peculiarities of lead. For example, the action of unstable lead tetrachloride on a diarylmercury would actually amount to the action of free chlorine, and not to an arylation reaction as in the case of germanium tetrachloride. When, however, in the reaction with diphenylmercury the lead tetrachloride is replaced by the fairly stable tetraacetate, the introduction of two aromatic radicals occurs:



By this method Kocheshkov and Nad [3] prepared organolead compounds of the class  $Ar_2PbX_2$  (X is the residue of an organic acid) having substituents in the aromatic nucleus, but they did not observe the formation of  $ArPb(OOCCH_3)_3$ .

Austin [4], following analogies from organomercury chemistry, attempted unsuccessfully to prepare  $ArPbX_3$  by the pyrolysis of lead tetrabenzoate:

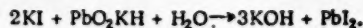


Methods based on disproportionation reactions in reverse have been applied successfully to aromatic tin compounds. It was by such a method that Kocheshkov [5] prepared members of the simplest class of organotin compounds  $ArSnX_3$  for the first time. However, the application of this method in organolead chemistry does not result in the synthesis of  $ArPbX_3$ . When diphenyllead diisobutyrate is treated with lead tetraisobutyrate, the latter is reduced to lead diisobutyrate.

Again, according to Meyer [6] compounds of the type  $RSnX_3$  can be prepared by the reaction



and Druce [7], following this analogy, attempted to prepare compounds of the type  $RPbX_3$ , but the process went in a different fashion:



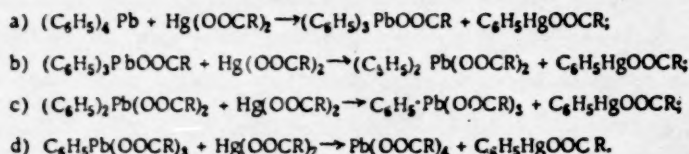
Lesbre [8], unlike Druce, found that Meyer's reaction could be applied to lead compounds and that in this way aliphatic compounds of the type  $RPbX_3$  (X is a halogen) could be prepared.

However, in 1948 Calingaert and coworkers [9] repeated Lesbre's experiments and were unable to reproduce his results. It is doubtful whether the use by Lesbre of boiling concentrated hydrochloric acid in the synthesis would allow the compound  $RPbX_3$  to remain undecomposed; it has been pointed out by several authors [10, 11] that such compounds are probably unstable to mineral acids. It is remarkable also that the compounds described by Lesbre were yellow, whereas all the compounds of the class  $ArPb(OOC\cdot R)_3$  that we have prepared are quite colorless (which is fully in accord with the well known lack of color in organic derivatives of quadrivalent lead).

Hence, after a critical examination of the data cited above, we considered it desirable to apply the reaction of dearylation with the aid of metal salts. In 1934, in a study of the action of mercuric chloride on various

organometallic compounds, including  $\text{Ar}_4\text{Pb}$ , we noted that the reaction is arrested at the stage of elimination of two aromatic radicals. "There are no signs that the reaction can be arrested at the stage of formation of  $\text{C}_6\text{H}_5\text{-PbCl}_2$ " [12]. This behavior was determined by the fact that the starting substance was diphenyllead dichloride, which is almost insoluble in organic solvents, and also by the fact that we were attempting to obtain  $\text{ArPbX}_3$  compounds that were genetically associated with unstable lead tetrachloride. It was therefore necessary to replace halogen by an organic acid residue and, as experiment showed, to use mild conditions (room temperature; all of the starting substances in solution).

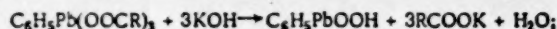
It was indeed found that, when a solution of a bivalent mercury salt in an organic acid was added to an organolead compound, also dissolved in an organic acid, the smooth elimination of one, two, three, or four radicals occurs, the number depending on the number of molecular proportions of mercury salt taken:



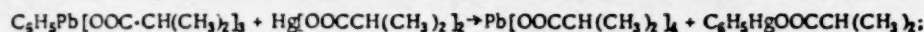
Our main concern was with the reaction of Equation (c) (the products obtained in (a) and (b) could be obtained in other ways).

It was shown by agreeing duplicate analyses that the products were pure and corresponded in composition to  $\text{ArPbX}_3$ . This structure was further confirmed by

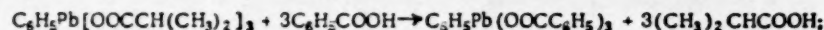
a) determining the number of acid groups (three):



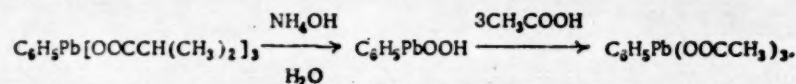
b) eliminating the last (fourth) phenyl group by treatment with one molecular proportion of mercury salt, which resulted in the formation of crystalline lead tetraisobutyrate:



c) converting phenyllead triisobutyrate into phenyllead tribenzoate by a reaction in which exchange of acid residues occurred:



d) converting phenyllead triisobutyrate by hydrolysis into benzenepiumbonic acid, and hence into phenyllead triacetate:



## EXPERIMENTAL

### Phenyllead Triacetate

Mercuric acetate (1.92 g = one molecular proportion) was warmed with 40 ml of glacial acetic acid, and the resulting solution was cooled to room temperature. Diphenyllead diacetate [3] (2.88 g = one molecular proportion) was then added; it rapidly went into solution. As reaction proceeded the amount of mercuric acetate present diminished, the change being followed by the following well known qualitative reaction: a drop of the solution was applied to a polished copper plate, and after a few seconds a dark spot appeared which became lighter when rubbed; from the intensity of the spot it was possible to get a rough idea of the concentration of unchanged mercury salt. After one day, when reaction was almost complete, 1.28 ml of alcoholic 4.7 N HCl (one molecular proportion) was added dropwise from a microburet in order to convert the phenylmercury acetate formed into phenylmercury chloride. The precipitate was filtered off and washed with alcohol. Its melting point was 253°, raised by crystallization from xylene to 258°, which corresponds to phenylmercury chloride; the yield was 1.6 g (80%). The filtrate was left in a vacuum desiccator over caustic potash until the acetic acid had evaporated away. The solid residue (3.63 g) was dissolved in 15 ml of hot dry freshly distilled ethyl acetate, and the solution was filtered. The filtrate was cooled in a mixture of salt and ice, and the crystals that separated were filtered off



under suction and washed with hexane. The yield of phenyllead triacetate, m.p. 101-102°, was 2.19 g (79%).

The product (1 g) was recrystallized from 6 ml of hot ethyl acetate and the crystals were washed with hexane and with ether, vacuum-dried for five minutes at 61° (jacket of chloroform vapor), and then exposed to a vacuum for a further 30 minutes at room temperature. They were then ground in a mortar and again subjected to the same drying procedure. The melting point of the product (0.5 g) was unchanged at 101-102°.

Found %: Pb 45.93; 45.17

$C_{12}H_{14}O_6Pb$ . Calculated %: Pb 44.92

**Determination of the Number of Acetate Groups.** A weighed amount (0.0649 g) of the substance was dissolved in alcohol and an excess of 0.1 N NaOH was added. Water was then added, and the excess of caustic soda was determined by titration with 0.1 N  $H_2SO_4$ . The volume of the caustic soda consumed in reaction with organolead compounds was found to be 4.45 ml (each acetate group corresponded to 1.41 ml of 0.1 N NaOH, and three acetate groups corresponded to 4.23 ml).

Phenyllead triacetate forms a loose mass of white needles resembling cotton wool. It is readily soluble in the cold in methanol, ethanol, chloroform, and acetic acid; it is moderately soluble in the cold in ethyl acetate and benzene, but dissolves readily when warmed with these solvents; it is of poor solubility in ether, and it does not dissolve in hexane even when heated.

#### Phenyllead Triisobutyrate

I. Yellow mercury oxide (2.16 g = one molecular proportion) was warmed with 9 ml of isobutyric acid, and the warm solution formed was cleared from slight turbidity by filtration. The filtrate was warmed with 5.32 g (one molecular proportion) of diphenyllead diisobutyrate [1], and the resulting solution was left in a dish over caustic alkali in a vacuum desiccator. After five days the precipitated crystals were filtered off and washed with cold hexane. The substance was dried in a vacuum for five minutes at 61° (jacket of chloroform vapor), and then exposed to a vacuum for not less than 30 minutes at room temperature. The yield of phenyllead triisobutyrate, m.p. 76.5-77.5°, was 2.5 g. The mother liquor was left in a vacuum desiccator, and a further 0.21 g of material of the same melting point was isolated. The total yield of phenyllead triisobutyrate was 2.71 g (48.8%). A portion (0.5 g) was recrystallized, with careful heating, from 3 ml of dry hexane. Well formed crystals separated and were washed with hexane and dried (0.4 g, m.p. 77-78°). A further recrystallization from hexane did not affect the melting point.

Found %: Pb 38.04; 37.85

$C_{18}H_{26}O_6Pb$ . Calculated %: Pb 37.99

The substance can be crystallized also from alcohol, but when the product is melted in a capillary a turbid melt is obtained.

II. Yellow mercuric oxide (2.16 g = one molecular proportion) was dissolved in 20 ml of isobutyric acid, and 5.32 g (one molecular proportion) of diphenyllead diisobutyrate was added; it dissolved readily. The reaction mixture was left for 12 days at room temperature. Phenylmercury chloride was separated as described above, and two thirds of the total amount of isobutyric acid was distilled from the filtrate at 2 mm and not above 40° (water bath). In the further treatment one of the following procedures was adopted. 1) The residue was transferred to a dish and left over caustic alkali in a vacuum desiccator. After eight days the precipitate formed was filtered off, washed with hexane, and dried as described above. The yield was 2.75 g (50.5%); m.p. 77-78°. 2) The residue was cooled in a mixture of ice and salt. The crystals that separated were filtered off and washed with hexane. The mother liquor was diluted with an equal volume of hexane and again cooled. The yield was somewhat lower with this procedure. Phenyllead triisobutyrate is a white crystalline substance, readily soluble in the cold in alcohol, acetone, chloroform, and benzene, and moderately soluble in the cold in hexane (readily soluble hot).

#### Phenyllead Tribenzoate

Phenyllead triisobutyrate (0.55 g = one molecular proportion) was added to a hot solution of 0.44 g (one molecular proportion + 20% excess) of benzoic acid in 8 ml of hexane. The solution was heated to the boil and set aside to crystallize. On the next day the precipitate formed was filtered off and washed successively with hot hexane, alcohol, and ether. The precipitate (0.4 g) was recrystallized from 1.5 ml of dry benzene, washed with hexane, and dried in a vacuum at 61° (jacket of chloroform vapor). The yield was 0.27 g (41.5%); m.p. 149.5-151°.

Found %: Pb 32.08; 32.07  
 $C_{27}H_{29}O_8Pb$ . Calculated %: Pb 32.01

Phenyllead tribenzoate is a white crystalline substance, readily soluble in the cold in chloroform, ethyl acetate, and benzene. In alcohol it is moderately soluble cold, but readily soluble hot. It is insoluble in ligroin and hexane.

#### Benzeneplumbonic Acid

A solution of 0.27 g of phenyllead triisobutyrate in 5 ml of absolute alcohol was added dropwise under vigorous stirring to 6 ml of 5% ammonia. Reaction proceeded without appreciable rise in temperature. A yellowish amorphous precipitate appeared immediately. When the addition was complete, stirring was continued for three hours, and the reaction mixture was then set aside overnight. The precipitate was filtered off, carefully washed with water, with alcohol, and with ether, and then dried in a vacuum at 100° for one hour. The product was carefully ground and then further subjected to the same drying treatment for 80 minutes. The yield was 0.15 g (88.5%).

Benzeneplumbonic acid is a yellowish amorphous substance. It burns with a flash and a smoky flame, forming the yellow incrustation of lead oxides that is characteristic for organolead compounds. It is readily soluble in the cold in dilute hydrochloric acid, and it dissolves with difficulty in excess of concentrated (40-50%) caustic soda.

Found %: Pb 64.99; 65.58  
 $C_8H_6O_2Pb$ . Calculated %: Pb 65.31

When dried as indicated above, benzeneplumbonic acid reacts gently with concentrated sulfuric acid (the first stage of analysis). When benzeneplumbonic acid that has not been dried sufficiently is mixed with sulfuric acid, it bursts into flame, and great care must therefore be taken in the early stages of mixing: a few drops of acid that has been cooled with ice and salt should first be added cautiously. When benzeneplumbonic acid is dried for a longer time, anhydride formation occurs. For example, after being dried under the same conditions for six hours, the material contains 66.47% of lead (the calculated amount for  $C_8H_6PbO \cdot O \cdot PbOC_6H_5$  is 57.22%).

Benzeneplumbonic acid is readily soluble both in mineral and in organic acids. Benzeneplumbonic acid (0.2 g) was ground in the cold with 0.34 g (a two-fold excess) of isobutyric acid, and the solution obtained was left over caustic alkali in a vacuum desiccator. On the next day a small crystal of phenyllead triisobutyrate was added, and the reaction mixture solidified completely. The crystals were recrystallized from hexane and then melted at 77-78°. Phenyllead triisobutyrate obtained by the arylation of diphenyllead diisobutyrate melted at 77-78°. The melting point of a mixture of these preparations was not depressed.

#### Conversion of Phenyllead Triacetate into Phenyllead Triisobutyrate via Benzenep- lumbonic Acid

A solution of 2 g of phenyllead triacetate in 30 ml of absolute alcohol was added dropwise with mechanical stirring to 50 ml of 5% ammonia. When addition was complete, the mixture was stirred for three hours and then set aside overnight. The precipitate formed was filtered off, washed successively with water, alcohol, and ether, and dried for one hour in a vacuum at 100°. The precipitate was ground in a mortar and then dried for one hour further under the same conditions. The yield was 0.9 g (66%).

A portion of the freshly prepared benzeneplumbonic acid (0.25 g = one molecular proportion) was ground with 0.24 g (3 molecular proportions + 15% excess) of isobutyric acid. The reaction mixture was diluted with benzene and filtered. The filtrate was transferred to a vacuum desiccator containing caustic alkali and paraffin wax (to remove solvents). The residue was a thick oil that crystallized out completely when a small crystal of phenyllead triisobutyrate was introduced. After one or two crystallizations from hexane, the substance melted at 77-78°. The previously prepared phenyllead triisobutyrate melted at 77-78°, and the melting point of a mixture of the two preparations was not depressed.

#### Some Properties of Phenyllead Triacetate and Triisobutyrate

When chloroform solutions of iodine and of either of these substances were mixed at room temperature, there was no decolorization and no decolorization occurred when the mixture was boiled for some time. When

the solution was left overnight, the color became weaker and a precipitate of lead iodide appeared, but even after 24 hours the solution still retained a definite feeble violet color. When phenyllead triacetate or triisobutyrate was boiled with water, hydrolysis occurred: the original crystalline material became amorphous, and the odor of the free organic acid appeared. At room temperature hydrolysis was slow. When the substance was left in the air for 5-6 days, its melting point became low and indefinite. The hydrolysis products (probably basic salts, which we have not yet investigated closely) readily passed into solution when 15-20% caustic alkali was added, and they also dissolved when acid was added; they did not dissolve in sodium carbonate solution, cold or hot. When phenyllead triacetate or triisobutyrate was hydrolyzed in the cold with 5% ammonia, the resulting freshly precipitated benzenepbumbonic acid dissolved smoothly in 15-20% caustic alkali - behavior that contrasts with that of the dried acid (see above), which dissolves with difficulty.

#### Dearylation of Phenyllead Triisobutyrate with the Aid of Mercuric Isobutyrate

Phenyllead triisobutyrate (0.55 g = one molecular proportion) was warmed with 1.2 ml of isobutyric acid, and the resulting solution was mixed with a solution of 0.217 g (one molecular proportion) of yellow mercuric oxide in 0.8 ml of isobutyric acid. Reaction was slow, and the copper test for mercuric isobutyrate was positive; when water was added to a drop of the solution, no lead dioxide separated (absence of lead tetraisobutyrate in the mixture). After four days the test for the presence of mercuric ions was still positive, but a brown turbidity due to lead dioxide now formed when a drop of the reaction mixture was mixed with water. Well formed crystals gradually formed on the bottom of the flask. After ten days the reaction mixture was cooled with ice, and the precipitate was filtered off and washed with hexane. The yield was 0.2 g (36%); m.p. 114°. The melting point of lead tetraisobutyrate is 114° (see below), and a mixture with known lead tetraisobutyrate showed no melting point depression. The substance decomposed in the air, and it gave a brown precipitate of lead dioxide with water. Even after it had stood for ten days, the mother liquor still contained some mercuric isobutyrate.

#### Lead Tetraisobutyrate

A mixture of 17.6 g (one molecular proportion) of lead tetraacetate and 70 g (20 molecular proportions - five times the theoretical amount) of isobutyric acid was heated in a water bath in a round-bottomed flask carrying a column and arranged for vacuum distillation. The pressure was 12-15 mm, and the temperature of the bath was raised gradually to 70°. The reaction was carried out both without passage of air through the capillary leak, and also with passage of air, which, in order to avoid hydrolysis, had been first passed through a Tishchenko bottle containing sulfuric acid. The acetic acid and part of the isobutyric acid distilled over slowly, about 36 ml (half of the total volume of reaction mixture) being collected. Well formed crystals of lead tetraisobutyrate separated from the residue, when cool. These were filtered off through a funnel carrying a sintered-glass filter and protected from atmospheric moisture. They were washed with a little isobutyric acid, and isobutyric acid was removed with petroleum ether. The yield of lead tetraisobutyrate was 19 g (85.5%); it melted at 113-114° (Colson [13] gives 109°).

After being washed with petroleum ether, the substance was sufficiently pure and did not require recrystallization. However, when too much isobutyric acid was distilled off, the lead tetraisobutyrate obtained had a low melting point, and it had to be recrystallized from petroleum ether with the addition of a few drops of isobutyric acid (1 g of lead tetraisobutyrate was heated with 4 ml of petroleum ether).

Found %: Pb 36.92

$C_{16}H_{24}O_8Pb$ . Calculated %: Pb 37.32

Lead tetraisobutyrate forms white crystals, and it is readily soluble in the cold in chloroform, dichloroethane, carbon tetrachloride, benzene, toluene, and xylene, but less soluble in isobutyric acid. It dissolves poorly in the cold, but readily when heated in petroleum ether and hexane; it is decomposed by water and by alcohol.

#### SUMMARY

1. By the dearylation of organolead compounds of formula  $Ar_2PbX_2$ , members of a new class of compounds,  $ArPbX_3$ , have been prepared for the first time (Ar is an aromatic radical, and X is the residue of an organic acid).
2. The properties and mutual transformations of phenyllead triacetate, phenyllead triisobutyrate, phenyllead tribenzoate, and benzenepbumbonic acid are described.

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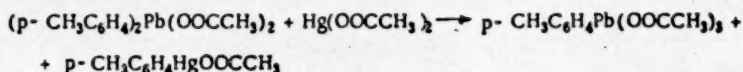
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# COMPOUNDS OF THE CLASSES $Ar_2PbX_2$ AND $ArPbX_3$ IN THE p-TOLYL SERIES

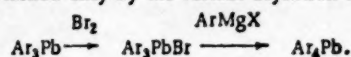
K. A. Kocheshkov and E. M. Panov

In the course of work on p-tolyl members of the new class of compounds  $ArPbX_3$  ( $Ar$  is an aromatic radical and  $X$  is the residue of an organic acid) which we have discovered [1]



we encountered difficulties associated with the synthesis of the starting substance  $Ar_2PbX_2$ .

It is stated in the literature [2] that di-p-tolyllead diacetate (or diformate) is formed by the action of the hot organic acid on tetra-p-tolyllead. It is known, however, that for phenyl homologs, compounds of the class  $Ar_4Pb$  can be obtained only by the further arylation of  $Ar_3Pb$  [3]:

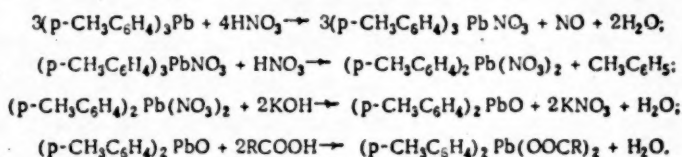


It would obviously be irrational for our purpose to make use of this reaction and combine it with subsequent elimination of two aryl groups. We therefore investigated several possible methods for the direct conversion of  $Ar_3Pb$  into  $Ar_2PbX_2$ .

1. The direct action of organic acids at 120-140° on tri-p-tolyllead (which probably underwent disproportionation  $4Ar_3Pb = 3Ar_4Pb + Pb$ ) gave only low yields.

2. Synthesis in accordance with the scheme  $(p-CH_3C_6H_4)_3Pb \xrightarrow{I_2} (p-CH_3C_6H_4)_3PbI_2 \xrightarrow{(p-CH_3C_6H_4)_2PbI_2} (p-CH_3C_6H_4)_2PbO \xrightarrow{CH_3COOH} (p-CH_3C_6H_4)_2Pb(OOCCH_3)_2$  has no advantage over the previous method, since the preparations of mono- and di-halides required separate stages. Moreover, the dihalides are of low solubility in organic solvents, and their conversion into the corresponding oxides is difficult.

3. We found that the most expedient method was as follows:



Unlike the corresponding dihalide, di-p-tolyllead dinitrate is soluble in hot alcohol and is readily converted by alcoholic caustic potash into the corresponding oxide, and then further into the salt  $Ar_2PbX_2$ .

In this way di-p-tolyllead diacetate (in 64% yield) and di-p-tolyllead diisobutyrate (in 48% yield) were prepared, and these substances were then applied in the preparation of p-tolyllead triacetate and p-tolyllead trimethacrylate.

## EXPERIMENTAL

### Di-p-tolyllead Diacetate

With constant shaking and over a period of 20-25 minutes 7.5 g (one molecular proportion) of tri-p-tolyllead [4] was added in small portions of 75 ml of concentrated nitric acid heated to the boiling point. Reaction was very vigorous -- each fresh portion of tri-p-tolyllead caused foaming of the mixture with evolution of brown oxides of nitrogen. The nitric acid turned yellow, and precipitate of di-p-tolyllead dinitrate formed on the bottom of the flask. When the whole of the tri-p-tolyllead had been added, heating was continued for a few minutes, and the reaction mixture was then cooled. The di-p-tolyllead dinitrate was filtered off and washed with water.

This crude di-p-tolyllead dinitrate was heated with 80 ml of alcohol, and the solution so obtained was brought to the boil. A solution of 2.2 g (two molecular proportions + 20% excess) of caustic potash in 25 ml of

ethanol was then added, and a yellowish precipitate formed, which was filtered off and washed successively with alcohol and ether. The product was 5.25 g of di-p-tolyllead oxide.

The unpurified di-p-tolyllead oxide (3.2 g) was mixed with 3 ml of glacial acetic acid (heat was evolved). In order to obtain more complete solution the mixture was warmed cautiously, but some undissolved material still remained. Ethyl acetate (15 ml) was added, and the mixture was heated to the boil and then filtered. The filtrate was cooled in a mixture of ice and salt, and 3.08 g (64% on the amount of tri-p-tolyllead taken) of di-p-tolyllead diacetate, m.p. 209-210°, was obtained. The substance was sufficiently pure: a further crystallization from ethyl acetate did not affect the melting point.

Found %: Pb 40.29; 40.67

$C_{18}H_{20}O_4Pb$ . Calculated %: Pb 40.84

Di-p-tolyllead diacetate is a white crystalline substance, m.p. 209-210° (Polis [2] gives 195°). It is extremely soluble in the cold in chloroform and acetic acid, and it is very soluble in ethanol and methanol. It is moderately soluble in the cold in benzene, acetone, and ethyl acetate, but is readily soluble at a higher temperature. It is of very poor solubility in hexane and ether, even when hot.

#### Di-p-tolyllead Diisobutyrate

1. A mixture of 1.2 g (one molecular proportion) of tri-p-tolyllead and 2.2 g (10 molecular proportions) of isobutyric acid was heated at 120-140° for one hour. The resulting solution (better after dilution with an equal amount of hexane) after cooling yielded well formed crystals (0.41 g) melting at 198-202°. Recrystallization from benzene raised the melting point to 202-203° (yield 0.3 g). A second crystallization from benzene did not affect the melting point.

Found %: Pb 36.96; 36.90

$C_{22}H_{28}O_4Pb$ . Calculated %: Pb 36.78

Determination of the Number of Acid Residues. For 0.0698 g of the substance, 2.85 ml of 0.1 N NaOH was required; 0.0698 g of di-p-tolyllead diisobutyrate is equivalent to 2.48 ml of 0.1 N NaOH.

2. A mixture of 4 g (one molecular proportion) of unpurified di-p-tolyllead oxide (see above) and 4 ml (about four molecular proportions) of isobutyric acid was prepared and was heated cautiously. Ethyl acetate (6 ml) was added, and the mixture was heated to the boil and then filtered from undissolved material. Crystals melting at 202-203° separated from the filtrate. In admixture with di-p-tolyllead diisobutyrate prepared as described above there was no depression of melting point. The yield was 2.7 g (48.3%).

Di-p-tolyllead diisobutyrate is extremely soluble in the cold in chloroform, and is very soluble in methanol, ethanol, and ethyl acetate. It is moderately soluble in the cold and very soluble at higher temperature in benzene, acetone, and carbon tetrachloride. It is insoluble in ether and hexane, even when hot.

#### p-Tolyllead Triacetate

Mercuric acetate (1.59 g = one molecular proportion) was warmed with 45 ml of glacial acetic acid, and to the resulting warm solution 2.5 g (one molecular proportion) of di-p-tolyllead diacetate (see above) was added; it dissolved very readily. After one day the copper-plate reaction for mercury ions was found to be negative. Drop-wise addition was then made of 1.9 ml of alcoholic 2.62 N HCl (one molecular proportion). The precipitate that formed was found to be p-tolylmercury chloride, m.p. 238° (Nesmeyanov [5] gives 238-239°); the yield was 1.5 g (86%). The filtrate was left over caustic alkali in a vacuum desiccator to remove acetic acid. The residue was a thick oil, which crystallized when rubbed out. The yield of crude material was 2-2.2 g; it was recrystallized from 6 ml of hot freshly distilled ethyl acetate acidified with a drop of acetic acid, the solution being filtered and cooled in an ice-salt mixture. The yield was 1.6 g (67%) of p-tolyllead triacetate, m.p. 84-86°, raised to 86-88° by a second crystallization from hot ethyl acetate; in further recrystallizations the melting point remained constant.

Found %: Pb 43.19

$C_{13}H_{16}O_6Pb$ . Calculated %: Pb 43.59

When crystallized from benzene, the substance separated with one molecule of solvent of crystallization.

The substance (1 g) was dissolved in hot benzene (3 ml). The solution was filtered and diluted with 3 ml of hexane. The crystals that separated (0.6 g) were vacuum-dried at 61° (jacket of chloroform vapor) for five minutes, and then at room temperature for 30 minutes.

Found %: Pb 37.60  
 $\text{CH}_3\text{C}_6\text{H}_4\text{Pb}(\text{CCCCCH}_3)_2\text{C}_6\text{H}_4\text{CH}_3$  Calculated %: Pb 37.49

The benzene of crystallization could be removed completely only by drying the finely ground material in a vacuum at room temperature for two days (Found %: Pb 43.44).

p-Tolyllead triacetate forms friable crystals, extremely soluble in the cold in methanol, ethanol, chloroform, and acetic acid. It is moderately soluble in the cold, and readily soluble at higher temperature, in ethyl acetate, acetone, and benzene; it is insoluble in hexane and ether, even when hot.

#### p-Tolyllead Trimethacrylate

p-Tolyllead triacetate (0.36 g = one molecular proportion) was dissolved in 1.5 ml of absolute alcohol, and the solution was filtered. Methacrylic acid (0.39 ml = six molecular proportions) was added to the filtrate, and the mixture was placed in ice and salt. After a few minutes well formed needles appeared, and these were filtered off and recrystallized from hexane. The yield was 0.17 g (42%).

Found %: Pb 37.31; 37.08  
 $\text{C}_{19}\text{H}_{22}\text{O}_6\text{Pb}$  Calculated %: Pb 37.44

At temperatures above 120° p-tolyllead trimethacrylate gradually decomposes without melting. It forms needle-like crystals, which are readily soluble in the cold in ethyl acetate, chloroform, and benzene. They are moderately soluble in the cold, and readily soluble at higher temperatures in methanol, ethanol, and acetone; they are poorly soluble in ether and hexane, even when hot.

#### p-ToluenepIumbonic Acid

A solution of 0.5 g of p-tolyllead triacetate in 10 ml of absolute alcohol was added dropwise with vigorous stirring to 12 ml of 5% ammonia. There was an immediate white amorphous precipitate. The reaction mixture was stirred for three hours and was then set aside overnight. The precipitated p-toluenepIumbonic acid was filtered off, carefully washed with water, with alcohol, and with ether (the substance yellowed somewhat on the filter), and then dried for one hour in a vacuum at 100°. The product was carefully ground and then dried further for one hour under the same conditions. The yield was 0.18 g (60%).

Found %: Pb 62.19; 62.52  
 $\text{C}_7\text{H}_6\text{O}_2\text{Pb}$  Calculated %: Pb 62.55

p-ToluenepIumbonic acid is a white or somewhat yellowish amorphous substance. It is readily soluble in the cold in dilute hydrochloric acid and also in organic acids; it dissolves with some difficulty in concentrated (40-50%) caustic alkali. When boiled with concentrated hydrochloric acid, it yields toluene (elimination of the tolyl group).

#### Conversion of p-Tolyllead Triacetate into p-Tolyllead Trimethacrylate via p-ToluenepIumbonic Acid

A solution of 0.5 g of p-tolyllead triacetate in 10 ml of absolute alcohol was added dropwise with vigorous stirring to 12 ml of 5% ammonia. There was an immediate white amorphous precipitate. The reaction mixture was stirred for three hours and was then set aside overnight. The precipitate formed was filtered off, washed with water, with alcohol, and with ether, and then dried in a vacuum at 100°. The freshly prepared p-toluenepIumbonic acid was ground with methacrylic acid, the mixture was diluted with benzene and filtered, and the filtrate was left in a vacuum desiccator to remove solvent. The residue was crystallized from hexane. The characteristic needles of the trimethacrylate were obtained.

Found %: Pb 37.08; 37.13  
 $\text{C}_{19}\text{H}_{22}\text{C}_6\text{Pb}$  Calculated %: Pb 37.44

#### SUMMARY

1. A method has been developed for the synthesis of compounds of the class  $\text{Ar}_2\text{PbX}_2$  (Ar is an aromatic radical and X is the residue of an organic acid) from  $\text{Ar}_2\text{Pb}$ , the syntheses investigated being those of di-p-tolyllead diacetate and di-p-tolyllead diisobutyrate.

2. Members of a new class of compounds have been prepared, namely, p-tolyllead triacetate and p-tolyllead trimethacrylate, the latter being obtained from the former by a transacylation process.

3. A new areneplumbonic acid has been described, namely. *p*-tolueneplumbonic acid.

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# FREE ENERGY CHANGE IN THE ADSORPTIONAL DISPLACEMENT OF BUTENE BY WATER FROM A CATALYST SURFACE

A. A. Balandin, O. K. Bogdanova, and A. P. Shcheglova

In the study of the action of catalysts it is important to know the properties of the intermediate adsorption complex formed between a reacting substance and the catalyst. Such properties include the adsorption coefficient of the substance for the catalytically active surface, and we have previously examined an experimental method for the determination of this property [1, 2].

The adsorption coefficient  $a$  is simply the adsorption equilibrium constant, and the quantity  $z$ , which has been called the relative adsorption coefficient, is the equilibrium constant for the adsorptional displacement of one substance by another from the active surface.

We shall denote the total number of like catalytically active centers on the given surface by  $s$ , and by  $s_0, s_1, s_2, \dots, s_n$  we shall denote the numbers of these centers in the free state ( $s_0$ ) and occupied each by a single molecule of the substances  $A_1, A_2, \dots, A_n$ , respectively, derived from the gas phase. The ratios

$$\left. \begin{aligned} N'_0 &= s_0/s \\ N'_1 &= s_1/s \\ N'_2 &= s_2/s \\ &\dots \\ N'_n &= s_n/s \end{aligned} \right\} \quad (1)$$

will be the mole fractions of free centers and adsorption complexes on the surface. By  $N_1, N_2, \dots, N_n$  we shall denote the mole fractions of the substances  $A_1, A_2, \dots, A_n$  in the gas, which has a total pressure of  $P$ , and by  $k_1, k_2, \dots, k_n$  we shall denote the rate constants for adsorption, and by  $k_{-1}, k_{-2}, \dots, k_{-n}$  the rate constants for desorption. For adsorption equilibrium, equating rates of adsorption and desorption, we have:

$$\left. \begin{aligned} k_1 N_1 P N'_0 &= k_{-1} N'_1 \\ k_2 N_2 P N'_0 &= k_{-2} N'_2 \\ &\dots \\ k_n N_n P N'_0 &= k_{-n} N'_n \end{aligned} \right\} \quad (2)$$

$$N'_0 + N'_1 + \dots + N'_n + N'_0 = 1 \quad (3)$$

It can be readily shown from Equation 2 that the adsorption equilibrium constants  $a_1, a_2, \dots, a_n$  are given by

$$\left. \begin{aligned} a_1 &= \frac{k_1}{k_{-1}} = \frac{N'_1}{N_1 N'_0} \cdot \frac{1}{P} \\ a_2 &= \frac{k_2}{k_{-2}} = \frac{N'_2}{N_2 N'_0} \cdot \frac{1}{P} \\ &\dots \\ a_n &= \frac{k_n}{k_{-n}} = \frac{N'_n}{N_n N'_0} \cdot \frac{1}{P} \end{aligned} \right\} \quad (4)$$

These adsorption equilibrium constants  $a_1, a_2, \dots, a_n$  are equal to the ratios of adsorption and desorption rate constants and refer, respectively, to the following dynamic equations:

$$\left. \begin{aligned} A_1(\text{gas}) + S(\text{surf.}) &= A_1 \cdot S(\text{surf.}) \\ A_2(\text{gas}) + S(\text{surf.}) &= A_2 \cdot S(\text{surf.}) \\ &\dots\dots\dots \\ A_n(\text{gas}) + S(\text{surf.}) &= A_n \cdot S(\text{surf.}) \end{aligned} \right\} \quad (5)$$

In these equations  $A_1 \cdot S$ ,  $A_2 \cdot S$ , ...,  $A_n \cdot S$  denote adsorption complexes. The quantities  $a_1$ ,  $a_2$ , ...,  $a_n$  can be regarded also simply as Langmuir adsorption coefficients. In fact, Equations 4 give

$$\left. \begin{aligned} N'_1 &= a_1 N_1 P N'_0 \\ N'_2 &= a_2 N_2 P N'_0 \\ &\dots\dots\dots \\ N'_n &= a_n N_n P N'_0 \end{aligned} \right\} \quad (6)$$

Associating with these the identity

$$N'_0 = N'_0 \quad (7)$$

and adding these equations (6 and 7), we find, with the help of Equation 3 that

$$1 = (a_1 N_1 P + a_2 N_2 P + \dots + a_n N_n P + 1) N'_0 \quad (8)$$

Determining the value of  $N'_0$  from Equation 8 and substituting it in the first of Equations 6, we arrive at Langmuir's isotherm for a mixture

$$N'_1 = \frac{a_1 N_1 P}{1 + a_1 N_1 P + a_2 N_2 P + \dots + a_n N_n P} \quad (9)$$

We find, therefore, that the equilibrium constants  $a_1$ ,  $a_2$ , ...,  $a_n$  are indeed adsorption coefficients.

As is well known, mole fractions, partial pressures  $p_i$  and concentrations  $[A]$  are related together, for each component of a gas mixture, by an equation of the type

$$N_1 P = p_{A_1} = [A_1] RT. \quad (10)$$

By substituting this in Equation 9 we can express the isotherm in other variables — partial pressures or concentrations. It should be noted that each term of the denominator (and also numerator) of Equation 9 is dimensionless, so that the dimensions of the constant coefficients in the terms of the denominator must be the inverse of those of the corresponding variables.

At sufficiently high pressures or concentrations we can neglect the term unity in the denominator of Equation 9. It will be obvious that the constant coefficients will retain their values irrespective of which variable,  $N$ ,  $P$ , or  $[A]$ , is chosen for the expression of the isotherm. Taking concentration as the variable we obtain

$$N'_1 = \frac{a_1 [A_1]}{a_1 [A_1] + a_2 [A_2] + \dots + a_n [A_n]} \quad (11)$$

Division of numerator and denominator by  $a_1$  yields

$$N'_1 = \frac{[A_1]}{[A_1] + z_2 [A_2] + \dots + z_n [A_n]} \quad (12)$$

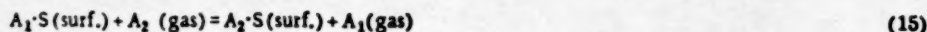
in which  $z_2$ , ...,  $z_n$  are dimensionless quantities, namely, relative adsorption coefficients:

$$\left. \begin{aligned} z_2 &= a_2 / a_1 \\ &\dots\dots\dots \\ z_n &= a_n / a_1 \end{aligned} \right\} \quad (13)$$

In order to bring out their physical meaning, we will substitute the values of  $a_1$ ,  $a_2$ , ...,  $a_n$  from Equation 4 into Equation 13:

$$z_2 = \frac{N_2 N_1}{N'_1 N_2} \quad (14)$$

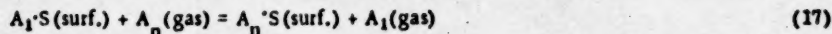
which is simply the equilibrium constant for the process of the adsorptional displacement of the substance  $A_1$  from the surface by the substance  $A_2$ :



and in general

$$z_n = \frac{N'_n N_1}{N'_1 N} \quad (16)$$

which is the equilibrium constant for the process



Since  $a_1, a_2, \dots, a_n$  and  $z_2, \dots, z_n$  are equilibrium constants, a treatment based on chemical thermodynamics will lead us to free energies.

It will be seen that the standard free energy for the formation of adsorption complexes from the substances  $A_1, A_2, \dots, A_n$  in the gas state and the free surface will be

$$\left. \begin{aligned} \Delta F^\circ(A_1) &= -RT \ln a_1 \\ \Delta F^\circ(A_2) &= -RT \ln a_2 \\ &\dots \dots \dots \\ \Delta F^\circ(A_n) &= -RT \ln a_n \end{aligned} \right\} \quad (18)$$

in which the free energies correspond line by line to the processes of Equation 5.

The standard free energies of displacement are

$$\left. \begin{aligned} \Delta F^\circ(A_2, A_1) &= -RT \ln z_2 \\ &\dots \dots \dots \\ \Delta F^\circ(A_n, A_1) &= -RT \ln z_n \end{aligned} \right\} \quad (19)$$

in which  $\Delta F^\circ(A_2, A_1)$  and  $\Delta F^\circ(A_n, A_1)$  refer to the processes of Equations 15 and 17, respectively.

It is of interest to note that the quantities  $z$  (owing to their zero dimensions), and also the free energies of displacement derived from them, are invariant quantities with respect to change of variable ( $N, P$ , or  $[A]$ ) and with respect to change in the units in which the adsorption coefficients are measured. On the other hand, in Equations 18, which involve  $a$ , such changes (if any desired pressures are considered) result in the appearance of constant terms, which determine the standard state.

Finding now from Equation 1 not the fraction of the surface  $N_1'$ , but the actual surface  $s_1$  occupied by the reacting substance  $A_1$ , and assuming the rate of reaction  $dx/dt$  to be proportional to the latter, we obtain the kinetic equation

$$\frac{dx}{dt} = k \frac{[A_1] + z_2}{[A_1] z_2 [A_2] + \dots + z_n [A_n]} \quad (20)$$

in which  $k$  is the rate constant for the catalytic reaction and includes the value of the active surface. It should be noted that in the derivation no limitation has been placed on the number of substances  $n$ .

Hence, by determining relative adsorption coefficients from kinetic measurements carried out by the method that we have developed [1], we are able to determine experimentally the standard free energies of displacement for the actual active catalytic centers (not merely for the total surface of the catalyst). Similarly, basing our calculations on Equation 9 instead of Equation 12, we may determine the standard free energies of adsorption on the catalytically active centers.

As an example of the application of these views, we consider below the effect of water vapor on the dehydrogenation of butene to butadiene. In a previous investigation [1] we have studied the kinetics of the catalytic dehydrogenation of butene to butadiene and have developed an experimental method that enables us to exclude a number of complicating factors from consideration, one of these being the ready polymerization of butadiene with the formation of a carbonaceous film that poisons the catalyst. It was found that the rate of dehydrogenation is not greatly dependent on pressure, the lowering of which reduces the rate of polymerization. The kinetic equation for the dehydrogenation reaction was found, and the relative adsorption coefficients were measured. It was found that the relation between the adsorption coefficients of butene, butadiene, and hydrogen at 560° could be expressed as 1 : 9.5 : 0.8. It was shown that the formula for the determination of adsorption coefficients actually did give fairly constant values of  $a$ , independent of concentrations.

In the present investigation it was first of all necessary to determine what type of poisoning occurred — permanent or temporary — when water vapor was introduced. If temporary, then the method of determining adsorption coefficients and free energies of adsorptional displacement could be applied, but if permanent, another approach would be required (see below).

## EXPERIMENTAL

The rates of dehydrogenation in various binary mixtures of butene and water vapor were measured. In order to determine the extent to which butadiene underwent decomposition, the behavior of binary mixtures of butadiene and water vapor was also studied, and other experiments were carried out on the dehydrogenation of butene over a catalyst that had been previously treated with water vapor.

### Experimental Procedure

The experiments were carried out by the flow method in the apparatus described previously [1], the only modification being the addition of a definite amount of water vapor to the butene (or butadiene) just before it entered the furnace. For this purpose, after passing through the flowmeter, gas from the gas holder entered a saturator containing water, which consisted of a cylinder provided with an electric spiral for the heating of the water, a thermometer, a buret containing water for the maintenance of the level in the saturator, and two tubes for entry and exit of gas. The gas from the saturator passed directly into a silica tube heated in an electric furnace. The exit gases from the furnace passed to a receiver fitted with a spherical condenser, in which the water vapor condensed, and were collected in a gas holder over saturated brine.

The temperature in the catalyst layer was measured by means of a nichrome-constantan couple contained in a silica pocket, the readings being taken on a potentiometer, and the temperature was maintained constant within  $\pm 0.25^\circ$ . The rate of passage of gas was determined by a flowmeter and was constant throughout an experiment. The degree of saturation of the butene (or butadiene) with water vapor was determined from the vapor pressure at the given temperature and, when possible, it was determined also from the weight of water collected in the receiver.

The experiments were carried out with 2 ml of chrome catalyst and 4 ml of silica (crushed quartz), which was placed in front of the catalyst to aid in the heating of the gas. After each experiment the catalyst was treated in a stream of air at  $600^\circ$ . Just before the experiment nitrogen was passed for three minutes in order to displace air from the apparatus. The sampling of gas for analysis was carried out three minutes after the beginning of the experiment.

The volumes of the gases were reduced to standard conditions. In the gas collected, butadiene was determined by its reaction with maleic anhydride, butadiene together with butene by absorption in 84% sulfuric acid, ethylene by absorption in a solution of mercuric sulfate in sulfuric acid, hydrogen and saturated hydrocarbons by combustion over copper oxide. In some experiments the exit gases were tested for carbon monoxide with ammoniacal cuprous chloride. Neither carbon monoxide nor carbon dioxide was detected in the gases, thus indicating that there was no chemical interaction between the hydrocarbons and water under the given conditions.

The butene was prepared from butyl alcohol and was purified by fractionation through a Davis column. The source of the butadiene was the butadiene fraction obtained from the SK works; it was purified from higher hydrocarbons and had the following composition: 90.8-91% of butadiene and 9-9.2% of butene.

### Experimental Results and their Discussion

The experiments with mixtures of butene and water vapor were carried out at  $560^\circ$ ,  $580^\circ$ , and  $600^\circ$  at a space velocity of 16,000 liters per liter per hour. The extent of dilution of butene with water vapor was varied from 9 to 75% by volume. The amount of butadiene formed under all these conditions was determined, and the reaction products were also analyzed by the methods indicated above. The results obtained are collected together in Table 1, in which they are arranged so that experiments at any given temperature are in order of increasing water content in the mixture. A control experiment was carried out at the end of every series.

Fig. 1 shows the dependence of the amount of butadiene formed in unit time (five minutes) on the composition of the butene-water mixture used. Fig. 2 shows similar results for the dependence of the amount of hydrogen formed on the composition of the original butene-water mixture. The corresponding curves of Figures 1 and 2 are very similar, indicating that the extent to which secondary decomposition reactions occurred was not great. The form of the curves indicates that water is adsorbed more strongly than butene. All of the curves fall below the additive



straight line. We applied the theoretical considerations that we developed in a previous paper [2] to the data obtained, and we calculated the relative adsorption coefficient of water molecules ( $\underline{z}$ ) from the formula derived from these considerations [1]

$$\underline{z} = \frac{\frac{m_0}{\underline{m}} - 1}{\frac{100}{p} - 1} \quad (21)$$

in which  $p$  is the mole percentage of butene in its binary mixture with water,  $m_0$  is the rate of dehydrogenation of pure butene, and  $\underline{m}$  is the same for the  $p\%$  mixture under the same conditions. Results of calculations from Equation 21 are given in the last column of Table 1.

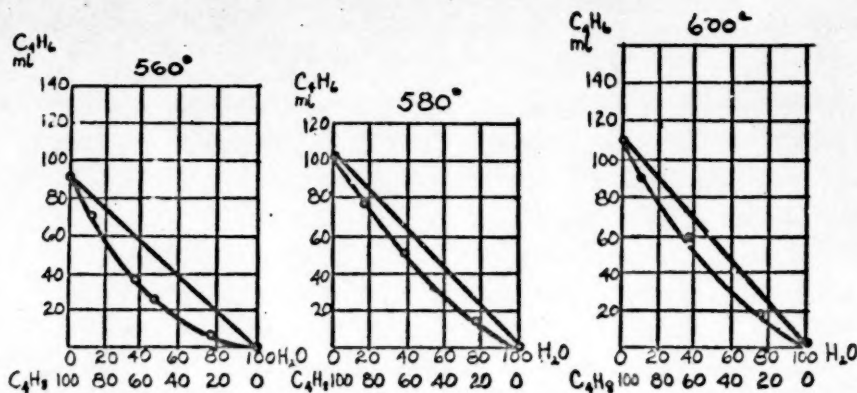


Fig. 1

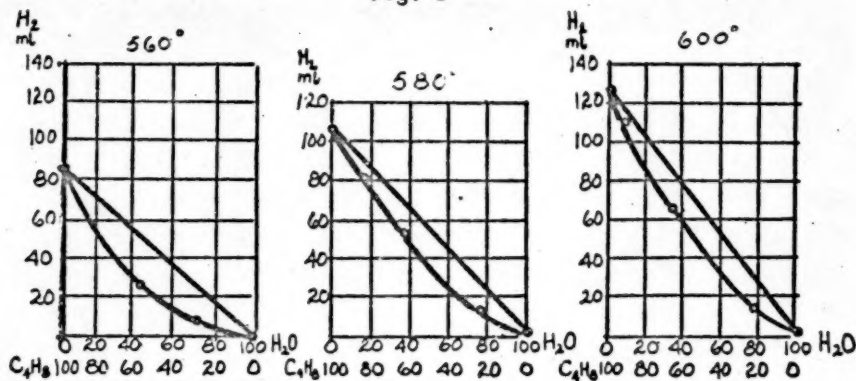


Fig. 2

It will be seen from Table 1 that in experiments at a given temperature the value of  $\underline{z}$  is fairly constant, thus confirming the applicability of the theory. With rise in temperature,  $\underline{z}$  falls; for a wide range of temperature we find that  $\underline{z}$  is 3.1 (for 560°) and 2.0 (for 600°). The rate of fall of  $\underline{z}$  apparently diminishes with rise in temperature, but the sensitivity of the method is such that over a narrower range of temperatures — 600° and 580° — the values of  $\underline{z}$  practically coincide. By the application of Equation 7 to these data we may find the free energy of the displacement of butene from the active surface by water. It is found that for this process

$$\Delta F^* = -4508 \text{ cal/mole at } 853^\circ K$$

$$\Delta F^* = -2702 \text{ cal/mole at } 853^\circ K$$

TABLE I  
2 ml of catalyst + 4 ml of crushed quartz; time of contact  $\tau = 0.06$  sec.

Experiment No.	Temperature of experiment (°C)	Composition of mixture (%) by volume		Analysis of gas (% by volume)*						Amount of $C_4H_6$ passed (ml)	Loss of $C_4H_6$ from 2 liters of mixture (ml)		Reaction products from 2 liters of mixture				Relative adsorption coefficient $\bar{z}$
		$C_4H_6$	$H_2O$	$C_4H_6 + C_4H_8$	$C_2H_4$	$C_2H_6$	$C_4H_8$	$H_2$	$C_nH_{2n+2}$				$C_4H_8$	$C_2H_4$	$H_2$	$C_nH_{2n+2}$	
832	600	100	-	89.80	1.6	5.5	5.8	1.0		1654	149	1130	35	128	22		
833	600	90	10	90.00	2.0	5.0	5.5	1.1		1863	230	92	37	108	20		2.2
834	600	63.7	36.3	90.6	1.6	4.6	4.6	1.1		1863	121	57	22	62	15		1.7
835	600	25.0	75.0	93.2	1.8	3.6	2.8	1.2		1793	32	16	9	14	5		2.0
836	600	100	-	90.0	2.0	5.4	5.2	0.9		2112	190	107	44	111	19		Mean 2.0
827	580	100	-	91.8	0.8	5.3	4.9	0.9		2045	141	103	17	105	19		
828	580	82	18	92.0	0.8	5.1	4.9	1.0		1839	156	77	13	82	17		(1.5)
829	580	63.5	36.5	93.4	0.8	4.2	3.7	0.9		1786	77	51	11	51	12		1.8
830	580	26.0	74	95.2	0.8	3.1	2.1	1.0		1737	20	14	4	11	5		2.0
831	580	100	-	93.2	1.0	4.9	3.8	0.8		2065	121	95	16	80	17		Mean 1.9
820	560	100	-	93.8	0.2	4.9	4.2	0.9		2090	133	93	4	88	19		
823	560	91	9	92.6	0.6	4.2	4.2	1.		1790	135	72	11	87	23		3.0
822	560	66.3	33.7	94.6	0.6	2.6	2.6	2.6		1760	74	38	8	61	13		3.2
824	560	65.0	35	94.4	0.8	2.9	2.9	0.9		1770	75	34	10	37	13		3.0
821	560	59	41	95.0	0.6	2.5	2.0	1.1		1900	62	26	7	24	16		3.5
825	560	29	71	97.2	0.6	1.3	1.1	0.6		1716	15	8	4	7	4		Mean 3.1
826	560	100	-	93.8	0.6	.3	4.4	0.8		2043	113	84	13	95	18		
837	560	100	-	95.2	0.4	4.6	3.1	0.8		2120	124	92	8	64	16		

\* No  $CO_2$  was found in the gas.

TABLE 2

2 ml of catalyst + 4 ml of crushed quartz; temperature 600°

Experiment No.	Dilution with water vapor		Composition of initial gas (ml)		Analysis of gas (% by volume)					Loss of $C_4H_6$ from 2 liters of mixture (ml)	Reaction products from 2 liters of mixture (ml)			
	Amount of hydrocarbons (%)	Amount of water (%)	$C_4H_6$	$C_4H_8$	$C_4H_6 + C_4H_8$	$C_2H_4$	$C_4H_6$	$H_2$	$C_nH_{2n+2}$		$C_4H_6$	$C_2H_4$	$H_2$	$C_nH_{2n+2}$
838	Without dilution		1930	192	96.8	0.8	81.5	0.6	0.8	538	61	12	9	12
840	93.2	6.8	1721	174	94.0	1.0	77.6	1.6	1.1	624	55	14	22	15
839	90.4	9.6	1707	173	95.8	1.0	78.2	1.4	0.9	547	78	13	19	13
841	68.3	31.7	1715	174	96.2	0.6	83.6	0.7	0.9	293	23	7	8	10
842	60.6	40.3	1662	168	97.2	0.4	86.8	-	1.1	156	3	5	-	14
843	25.0	75.0	1670	170	97.8	0.2	88.6	-	1.1	10	-	2	-	5

TABLE 3

2 ml of catalyst + 4 ml of crushed quartz; temperature 580°

Experiment No.	Dilution with water vapor		Composition of initial gas (ml)		Analysis of gas (% by volume)					Loss of $C_4H_6$ from 2 liters of mixture (ml)	Reaction products from 2 liters of mixture (ml)				
	Amount of hydrocarbons (%)	Amount of water (%)	$C_4H_6$	$C_4H_8$	$C_4H_6$	$C_2H_4$	$C_4H_6$	$H_2$	$C_nH_{n+2}$		$C_4H_6$	$C_2H_4$	$H_2$	$C_nH_{n+2}$	
827	Without dilution		2045	11	91.8	0.8		5.3	4.9	0.9	141	103	17	105	19
828	82.0	18	1839	9	92.0	0.8		5.1	4.8	1.0	185	94	16	99	21
846	Without dilution		1895	11	93.2	0.8		5.6	4.8	0.9	184	104	17	100	18
															with preliminary treatment with water vapor

In a similar way, applying the same formula (Equation 7) to the results obtained previously [1] ( $z_1 = 9.5$  for equilibrium constants for the displacement of butene by butadiene, and  $z_2 = 0.82$  for the displacement of butene by hydrogen (at 560°)), we find that the free energies of the adsorptional displacement of butene by butadiene and of butene by hydrogen are given, respectively, by

$$\Delta F_1^* = -8572 \text{ cal/mole}$$

$$\Delta F_2^* = -755 \text{ cal/mole}$$

The results show that, owing to adsorptional displacement water vapor should retard the dehydrogenation of butene to butadiene. The adsorption coefficient of water on the active centers of the dehydrogenation catalyst is found to be 2.0-3.1 times as great as that of butene. Rise in temperature should accelerate the dehydrogenation of butene, not only as a result of the usual increase in rate constant with temperature, but also as a result of the reduction in the value of  $z = p_{\text{H}_2\text{O}}/p_{\text{C}_4\text{H}_6}$ . All this is in accord with the experimental facts.

The theory is therefore applicable quantitatively for catalytic dehydrogenation centers. Temporary poisoning does indeed occur in the process under consideration. Dehydrogenation, however, is not the only reaction promoted by the catalyst: there are other active centers on the surface [3], and on these occur the polymerization and decomposition of butadiene with formation of products giving a carbonaceous film. These reaction products slowly migrate to the dehydrogenation centers and cause poisoning that is no longer temporary, but permanent. It is therefore necessary to consider also the action of water vapor on the complicating reactions accompanying dehydrogenation. This action is fairly complicated.

When the results are applied to the determination of the amount of butene decomposed in its relation to the water content of the mixture, we obtain the curves shown in Fig. 3. It will be seen that the addition of 10% of water vapor causes the decomposition to be greater than that of pure butene, but as the dilution of butene with water is increased further the extent of decomposition diminishes and, at 70-75%, becomes less than one-half of that found for pure butene.

Thus, the curve for the total amount of butene decomposed passes through a maximum at 10% of water. As the temperature rises, this maximum becomes higher. Analysis of the reaction products showed that in the region of the maximum there was a small rise in the content of saturated hydrocarbons. This rise, however, can be neglected, for the principal by-products are liquid polymerization and, possibly, dimerization products. With increased dilution the amount of liquid products diminishes. In the gaseous products — apart from butadiene, butene, and hydrogen-ethylene (0.4-2.0%) and saturated hydrocarbons (0.8-2.0%) were found. The distribution of the reaction products at different temperatures can be seen from Fig. 3.

Further experiments were carried out with mixtures of butadiene and water vapor (Table 2). The extent of dilution with water vapor was varied over almost the same range as in the case of butene, namely 6-75% by volume. The rate of passage was as before. The experiments were carried out at 600°. Like butene, butadiene gave a decomposition peak at about 10% of water. With increase in dilution, the extent of decomposition decreased. The main decomposition products of butadiene were liquids. In the exit gases small amounts of ethylene (up to 1%), hydrogen (0-1.6%), and saturated hydrocarbons (0.8-1.3%) were detected.

The experiments with butadiene show quite clearly that in the presence of a chrome catalyst small amounts of water vapor encourage the formation of liquid reaction products — products of the condensation of butadiene. This is a new fact, deserving of further study. At a higher content of water vapor, the water molecules cover the catalyst surface, screening the active centers, and they distribute themselves over the surface between the butadiene molecules. As a result, polymerization and dimerization are retarded, for these processes require the proximity of two butadiene molecules on the surface.

Hence, in the process under consideration on the given catalyst water vapor acts in several directions. First, reversible poisoning occurs: a) water displaces butene from the surface, which is unfavorable for the dehydrogenation of butene; b) water displaces butadiene (from other sites on the surface), which is favorable for dehydration since polymerization is suppressed. Second, as a result of the last effect, water suppresses the irreversible poisoning of the active dehydrogenation centers by polymerization products. Third, at low water concentrations an interesting phenomenon is observed — increased formation of liquid reaction products.

To determine the effect of water vapor on the catalyst surface, we carried out a pretreatment in which the catalyst was saturated with vapor. Just before the experiment nitrogen containing 10% of water vapor was passed over the catalyst for eight minutes. The mixture of butene and water vapor was passed for three minutes, and this was followed by undiluted butene that had been dried over calcium chloride. The results showed that this preliminary treatment with water vapor had no apparent effect on the catalyst surface. As will be seen from Table 3,



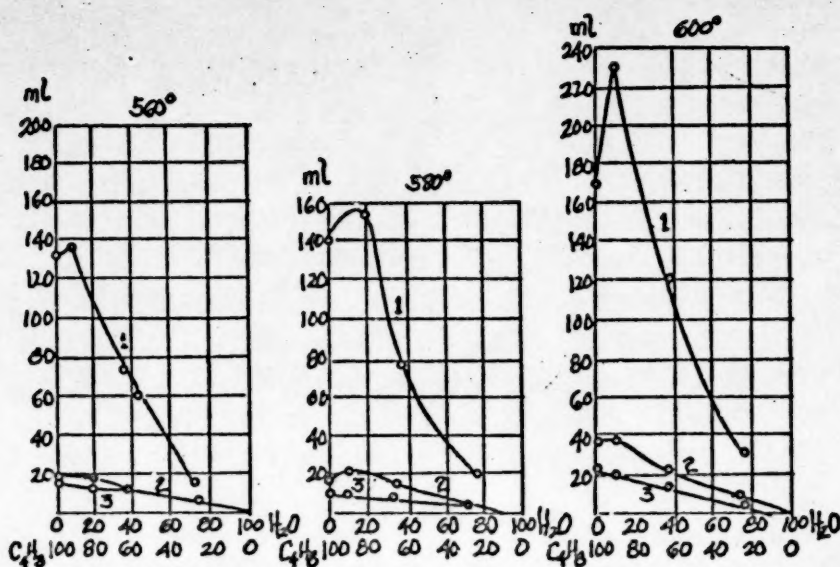


Fig. 3. 1)  $C_4H_6$ ; 2.) saturated hydrocarbons; 3.)  $C_2H_4$ .

Experiment 846, which was carried out at 580°, gave the same results as an experiment in which there was no preliminary treatment with water vapor. Hence, water vapor does not produce any irreversible poisoning or other change in the given catalyst.

#### SUMMARY

1. A method is proposed for the determination of equilibrium constants for the adsorptional displacement of some substances by others from a catalytically active surface; it yields also the free energies of the processes, and these determine the stability of the intermediate adsorption complexes.

2. It has been found that water vapor effects the adsorptional displacement of butene from the catalyst surface. The relative adsorption coefficient is about 3.1 at 560° and diminishes with rising temperature, attaining the value of 2.0 at 600°. The free energy of displacement of butene by water from the active catalyst surface is -4308 cal/mole at 833° K. and -2702 cal/mole at 853° K. Moreover, water vapor suppresses the conversion of butadiene into polymerization products, which give resinous films on the catalyst and so poison it irreversibly.

3. We have observed an interesting, previously undescribed example of the acceleration of the condensation of butadiene on the catalyst surface under the influence of small addition (about 10%) of water vapor. It was established that, under these conditions, water vapor itself would not bring about irreversible poisoning of the catalyst.

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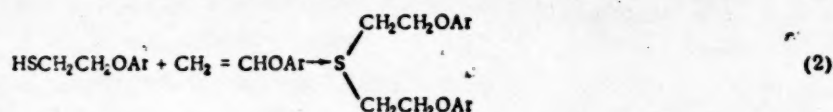
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**SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE**  
**COMMUNICATION 12. THE MOST EFFECTIVE CATALYSTS FOR THE ADDITION OF**  
**HYDROGEN SULFIDE TO VINYL ETHERS IN THE DIRECTION**  
**CONTRARY TO MARKOVNIKOV'S RULE**

M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro

With the object of developing a simple method for the synthesis of 2-aryloxyethanethiols and bis-(2-aryloxyethyl) sulfides, we have extended the reaction of anomalous addition of hydrogen sulfide to vinyl ethers, which we have previously studied for alkyl vinyl ethers [1, 2], to reactions with aryl vinyl ethers:



The ethers investigated were phenyl vinyl ether and p-tert-butylphenyl vinyl ether.

The reaction proceeded very slowly with these ethers, and the catalysts that we had used in the previous investigations — traces of oxygen, a solution of HCl in dioxane — were found to be very ineffective. Also, long heating at fairly high temperatures did not give a satisfactory yield of the reaction products. When we carried out the reaction with alkyl vinyl ethers in presence of these catalysts [2], the products were 2-alkoxyethanethiol and a mixture of bis(2-alkoxyethyl) sulfide and 1-alkoxyethyl 2-alkoxyethyl sulfide in various proportions. This indicated that some of the hydrogen sulfide molecules added to the vinyl ether in the direction required by Markovnikov's rule. Aryl vinyl ethers, however, showed specific behavior in this reaction: unlike alkyl vinyl ethers, they reacted, under comparable conditions, exclusively in the direction contrary to that required by Markovnikov's rule, with formation of the pure isomers indicated in Equations 1 and 2.

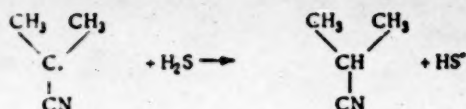
In earlier work Shostakovsky and Bogdanova have shown that the reactivity of aryl vinyl ethers in reactions proceeding under the influence of ionic catalysts is considerably less than that of alkyl vinyl ethers. For phenyl vinyl ether, for example, it is more difficult to effect hydrolysis and hydrohalogenation [3, 4], addition of alcohols, and the decomposition of its  $\alpha$ -halogen derivatives [5]. Aryl vinyl ethers are considerably less active in polymerization reactions in presence of ionic catalysts [6, 7]. We have recently shown [8] that the polymerization of aryl vinyl ethers can be brought about by radical catalysts, though the yield is very low.

The results of the work cited above and of our work in the present investigation show beyond doubt that, irrespective of the mechanism by which they proceed, the addition reactions of aryl vinyl ethers are much slower than the corresponding reactions of alkyl vinyl ethers.

It was considered to be necessary to find other catalysts of the radical type to accelerate the anomalous addition of hydrogen sulfide to aryl vinyl ethers. First of all we tried ascaridole, which has been shown to accelerate reaction with butyl vinyl ether greatly, even at room temperature [1]. With this catalyst only phenyl vinyl ether gave a satisfactory yield of reaction products.

It was found that the most effective catalyst was 2,2'-azobis[2-methylpropionitrile], which is well known as an extremely active initiator for free-radical polymerization processes — it was in the presence of this catalyst that radical polymerization of vinyl ethers was first effected [9]. As regards the use of the azo nitrile as a catalyst in free-radical addition reactions, the only literature reference is in a patent [10] relating to reaction between olefins and hydrogen sulfide.

2,2'-Azobis[2-methylpropionitrile] decomposes in a known manner [11] into free radicals. In our case such a radical will probably attack hydrogen sulfide, and a chain reaction will begin, the first stage of which may be represented as



The thiol radical so formed will then enter into the process in accordance with the scheme given in one of our earlier communications [1].

Unlike ascaridole, 2,2'-azobis[2-methylpropionitrile] can be used to effect the quantitative addition of hydrogen sulfide, not only to phenyl vinyl ether, but also to p-tert-butylphenyl vinyl ether, so that 2-aryloxyethane-thiols and bis(2-aryloxyethyl) sulfides can be synthesized in a comparatively simple way from readily accessible materials.

TABLE 1

Effect of Various Catalysts on the Addition Reaction between Hydrogen Sulfide and Butyl Vinyl Ether

Experiment No.	Amount of H <sub>2</sub> S (moles per mole of ether)	Experimental conditions					Unchanged ether (%)	Yield of reaction products (% on ether that reacted)			Content of 1,2'-isomer in sulfide fraction (%)
		Catalyst		Duration of experiment (days)	Temp-erature during heating (°C)	Duration of heating (hours)		Thiol	Sul-fide	Total	
		Name	Amount (% by weight on ether)								
103	0.3	Oxygen	Traces	2	-	-	98	-	-	-	-
31	0.5	"	"	13	-	-	35.4	27.7	6.27	90.4	2.5
14	1.0	"	"	7	60	30	-	52.6	43.4	96.0	20.0
26	0.4	HCl in dioxane	0.09	2	-	-	49.5	15.2	70.7	85.9	9.0
3	1.3		0.1	1	70	8	-	54.3	36.8	91.1	31.8
101	2.1	Ascarid-ole	1.5	2	-	-	6.0	77.0	13.8	90.8	1.5
94	0.4	Azo-nitrile	0.2	2	-	-	37.0	23.8	74.5	98.3	-
95	0.4		0.2	2	60	14	19.0	-	98.0	98.0	-
93	2.2		0.2	2	-	-	-	79.0	12.8	91.8	2

TABLE 2

Effect of Various Catalysts on the Addition Reaction between Hydrogen Sulfide and Cyclohexyl Vinyl Ether

Experiment No.	Amount of H <sub>2</sub> S (moles per mole of ether)	Experimental conditions					Unchanged ether (%)	Yield of reaction products(% on ether that reacted)			Content of 1,2'-isomer in sulfide fraction (%)
		Catalyst		Duration of experiment, (days)	Temperature during heating (°C)	Duration of heating (hours)		Thiol	Sulfide	Total	
		Name	Amount (% by weight on ether)								
1	1.2	Oxygen	Traces	150	-	-	33.3	65.8	20.3	86.1	88.6
10	1.0		-	35	60-65	245	-	16.5	48	64.5	91.7
4	0.9	HCl in dioxane	0.08	12	60	63	-	19.7	37.4	57.1	104.4
13	1.5	Ascarid-ole	1.0	7	60-62	37	-	70.3	23.5	93.8	20.4
14	0.5		1.0	7	60-62	45	50	30.5	55.2	85.7	13.1
11	1.2	Azo-nitrile	0.2	7	-	-	-	28.9	67.5	95.4	5.8
12	0.5		0.2	7	60-62	37	7.3	-	89.6	89.6	2.3



TABLE 3

Addition of Hydrogen Sulfide to Phenyl Vinyl Ether

Experi- ment No.	Amount of H <sub>2</sub> S (moles per mole of ether	Experiment conditions					Unchang- ed ether (%)	Yield of reaction products % on ether that reacted		
		Catalyst		Dura- tion of experi- ment (days)	Conditions of heating			Thiol	Sulfide	Total
		Name	Amount		Time (hours)	Temp- erature (°C)				
1	0.9	Traces of oxygen		70	Room		89.2	70.0	-	70
5	0.9	HCl in dioxane	0.02 ml	8	{ 40 40	60	36	44.8	46.6	91.4
6	0.6		"	0.02 ml		15	{ 122 120	60 35	39	24.6
7	2.2	Ascaid- ole	0.21 g	8	Room		99	-	-	-
10	2		0.2 g	5	34	60	45	75.8	15.9	91.7
8	0.9		0.2 g	16	53	60	41	40.3	47.6	87.9
9	2.1	Azo- nitrile	0.04 g	16	53	60	-	62.4	32.0	94.4

TABLE 4

Addition of Hydrogen Sulfide to p-tert-Butylphenyl Vinyl Ether

Experiment No.	Amount of H <sub>2</sub> S (moles per mole of ether)	Experiment conditions					Unchanged ether (%)	Yield of reaction products, % on ether that reacted		
		Catalyst		Duration of experiment (days)	Conditions of heating			Thiol	Sulfide	Total
		Name	Amount		Time (hours)	Temperature (°C)				
3	2.1	Ascaridole	0.3	10	52	60	94.5	-	-	-
2	4.2	Azo nitrile	0.05	35	Room		55.8	26.6	70.2	96.8
1	0.9		0.05	9	52	60	7.6	19.2	73.0	92.2
5	2.1		0.03	8	55	60	-	36.3	53.5	89.8

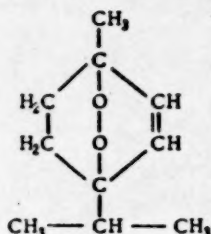
The characteristic behavior of the azo nitrile as an active radical catalyst is shown in the reaction of hydrogen sulfide with alkyl vinyl ethers, which are well known for their great tendency to combine with reagents of the type  $HX$  by an ionic mechanism. Tables 1 and 2 give comparisons of experimental material obtained for two alkyl vinyl ethers in presence of all of the catalysts that we studied. In presence of traces of oxygen and of a solution of  $HCl$  in dioxane the yield of addition products formed in accordance with Markovnikov's rule was fairly high for some alkyl vinyl ethers (for example, for cyclohexyl vinyl ether). The application of the azo nitrile enabled the extent to which the normal reaction occurred to be reduced to a minimum and was equally effective for all alkyl vinyl ethers, including cyclohexyl vinyl ether. It is probable that the azo nitrile was the most effective catalyst because it promoted rapid anomalous addition to a greater extent than other catalysts.

2,2'-Azobis[2-methylpropionitrile] can be recommended as a universal catalyst for the reaction of anomalous addition between hydrogen sulfide or a thiol and a vinyl ether of any structure.

## EXPERIMENTAL

The addition of liquid hydrogen sulfide to vinyl ethers was carried out by the procedure and under the conditions that we have described in detail in previous papers [1, 2].

Catalysts: 2,2'-Azobis[2-methylpropionitrile] was recrystallized from methanol and melted at  $104^\circ$ . Ascaridole



was prepared from Soviet chenopodium oil. A wide ascaridole fraction was collected (60-70% of raw material; b.p.  $90-93^\circ/7\text{mm}$ ). After refractionation, the ascaridole was purified by a method given in the literature [12], which consisted in two crystallizations from pentanesolution at  $-60$  to  $-70^\circ$  and distillation of the frozen-out fraction. The purified ascaridole had the following constants: b.p.  $91^\circ$  (7 mm),  $84.5-85^\circ$  (5.7 mm);  $n_D^{20}$  1.4740. The analysis was carried out by the iodometric method described in the same paper [12]. The ascaridole content was 99.8-100.2%.

The amounts of catalyst taken were 0.2% of the azo nitrile and 1% of ascaridole on the weight of vinyl ether. In Tables 1-4 the yields are calculated on the amount of ether that reacted, not on the amount taken. The total yield does not therefore give an indication of the extent to which reaction occurred, but only of the relative amounts of products in the given experiment.

### 1. Addition of Hydrogen Sulfide to Aryl Vinyl Ethers

1. Phenyl Vinyl Ether and Hydrogen Sulfide. The phenyl vinyl ether was purified by the method described previously [13], and it had the following constants: b.p.  $155-156^\circ$  (760 mm);  $n_D^{20}$  1.5225;  $d_4^{20}$  0.9767.

Data relating to the experiments on the addition of hydrogen sulfide to phenyl vinyl ether in presence of various catalysts are given in Table 3. The amount of ether taken varied from 15 to 25 g. Two of the experiments are described in detail below: in one of these the catalyst was  $HCl$  in dioxane, and in the other it was 2,2'-azobis[2-methylpropionitrile].

Experiment 6 (conditions given in Table 3). The substances taken were 25 g of the ether, 4.2 g of hydrogen sulfide (0.6 mole per mole of ether), and 0.02 ml of  $HCl$ -dioxane. The tube was opened after 15 days, which included 122 hours at  $60^\circ$  and 120 hours at  $35^\circ$ . After removal of uncombined hydrogen sulfide, the increase in weight of the reaction mixture was 2.8 g. Fractionation yielded the following fractions:

Fraction I B.p.  $30-32^\circ$  (4 mm);  $n_D^{20}$  1.5210; 9.8 g

Fraction II B.p.  $94-95^\circ$  (4 mm);  $n_D^{20}$  1.5630; 4.8 g

The residue, which was completely colorless, crystallized (11.3 g).

Fraction I was unchanged phenyl vinyl ether. After refractionation, Fraction II came over entirely at 94-95° (5 mm); it was 2-phenoxyethanethiol  $C_6H_5OCH_2CH_2SH$ , b.p. 96-97° (4.5 mm); 106-108.5° (7.5 mm);  $n_D^{20}$  1.5610;  $d_4^{20}$  1.1027; found MR 45.29; calculated MR 44.88.

Found %: C 62.44 62.38; H 6.44; 6.61; S 20.60; 20.88  
 $C_6H_9OS$ . Calculated %: C 62.30; H 6.54; S 20.79

When treated with alcoholic mercuric chloride, the thiol gave the mercurichloride  $C_6H_5OCH_2CH_2SHgCl$ , which crystallized from boiling alcohol in the form of fine threadlike crystals, the melting point of which was indefinite. It was recrystallized from boiling xylene.

Found %: C 24.58; 24.30; H 2.34; 2.49  
 $C_6H_5OSHgCl$ . Calculated %: C 24.68; H 2.33

For 2-phenoxyethanethiol the literature gives b.p. 112° (7.5 mm) [14]; b.p. 134° (29 mm);  $n_D^{25}$  1.5597 [15]. In the first of these investigations the thiol was synthesized by the condensation of 2-phenoxyethyl halide with hydrogen sulfide in presence of sodium ethoxide, and in the second it was obtained by a complex multistage synthesis from substances that are not readily accessible.

The crystalline sulfide fraction was distilled from a pear-shaped flask, when it came over at 181-183° (1.5-1.8 mm). After recrystallization from warm ethanol the sulfide melted at 54-55°.

Found %: C 69.96; 69.91; H 6.67; 6.80; S 11.59; 11.44  
 $C_{16}H_{14}S_2$ . Calculated %: C 70.04; H 6.61; S 11.66

The sulfide contained none of the isomeric monothioacetal  $CH_3CH(OC_6H_5)SCH_2CH_2OC_6H_5$  as impurity, for its alcoholic solution did not give the reaction, characteristic for this class of substances, with alcoholic mercuric chloride in presence of Methyl orange [16]; it therefore consisted of bis(2-phenoxyethyl) sulfide  $(C_6H_5OCH_2CH_2)_2S$ . The literature gives a melting point of 54.2° for this sulfide, which was prepared by the condensation of mustard gas with sodium phenoxide [17].

Experiment 9 (conditions given in Table 3). The substances taken were 20 g of phenyl vinyl ether, 12 g of hydrogen sulfide (2.1 moles per mole of ether), and 0.04 g of 2,2'-azobis[2-methylpropionitrile]. After 16 days, which included a period of 53 hours at 60°, the tube was opened. The increase in weight was 4.2 g. No unchanged phenyl vinyl ether could be detected. Fractionation yielded 16 g of pure 2-phenoxyethanethiol, b.p. 96-100° (4-4.5 mm) and  $n_D^{20}$  1.5600, i.e. having constants close to those already given for this substance (Experiment 6). The residue remaining after removal of the thiol fraction was transferred while hot to a tared weighing bottle, in which it crystallized (7.2 g). After a single recrystallization from warm alcohol it melted at 54.5-55°, which corresponds to bis(2-phenoxyethyl) sulfide. Thus, the use of the azo nitrile greatly increased the rate at which hydrogen sulfide added to phenyl vinyl ether.

2. p-tert-Butylphenyl Vinyl Ether and Hydrogen Sulfide. The p-tert-butylphenyl vinyl ether had b.p. 88.5-89° (6 mm); 80.5-81.5° (4.5 mm);  $n_D^{18}$  1.5090. The experiments on the addition of hydrogen sulfide to p-tert-butylphenyl vinyl ether were carried out with 15-25 g portions of the ether; the data are given in Table 4. Only ascaridole and 2,2'-azobis[2-methylpropionitrile] were used as catalysts. It was not considered to be desirable to try less effective catalysts, since even ascaridole did not bring about the addition of hydrogen sulfide to p-tert-butylphenyl vinyl ether after a long period of heating.

Experiment 5 (conditions given in Table 4). The substances taken were 15 g of the ether, 6 g of hydrogen sulfide (2.1 moles per mole of ether), and 0.03 g of 2,2'-azobis[2-methylpropionitrile]. Vacuum fractionation of the products yielded 8 g of a substance boiling at 132-134° (4 mm). The greenish viscous liquid remaining in the distilling flask was transferred while hot to a tared weighing bottle, in which it crystallized as it slowly cooled (8 g).

Redistillation of the liquid fraction yielded:

Fraction I. b.p. 120-130-142° (7 mm); 0.5 g  
 Fraction II. b.p. 142-143° (7 mm); 6.5 g

The residue from this distillation (0.8 g) crystallized.

Fraction II, a colorless evil-smelling liquid, had the following constants after refractionation: b.p. 134-134.5 (4.5 mm);  $n_D^{20}$  1.4536;  $d_4^{20}$  1.0206; found MR 64.12; calculated MR 63.35.

Found %: C 68.63 68.45; H 8.72; 8.63; S 15.33; 15.33  
 $C_{12}H_{18}OS$ . Calculated %: C 68.52; H 8.63; S 15.25

The substance corresponded in analysis to 2-p-tert-butylphenoxyethanethiol  $C_{10}H_{13}OCH_2CH_2SH$ ; it was obtained in 36.3% yield.

It was converted by alcoholic mercuric chloride into its mercurichloride  $C_{10}H_{13}OCH_2CH_2SHgCl$ , which was recrystallized twice from boiling alcohol and then melted with decomposition at 207°.

Found %: C 32.69 32.68; H 4.03; 4.00; Cl 7.74; 7.86  
 $C_{12}H_{17}OSHgCl$ . Calculated %: C 32.36; H 3.85; Cl 7.96

After recrystallization (twice) from very small amounts of alcohol, the crystalline sulfide fraction no longer had any odor. It melted at 43.5°.

Found %: C 74.55; 74.63; H 8.90; 8.82; S 8.48; 8.53  
 $C_{14}H_{24}O_2S$ . Calculated %: C 74.56; H 8.87 S 8.30

The sulfide did not give the qualitative reaction for the isomeric monothioacetal, and was therefore pure bis(2-p-tert-butylphenoxyethyl) sulfide ( $C_{10}H_{13}OCH_2CH_2$ )<sub>2</sub>S, obtained in 53.5% yield.

## II. Addition of Hydrogen Sulfide to Alkyl Vinyl Ethers

Tables 1 and 2 give comparisons of the results of experiments on the addition of hydrogen sulfide to butyl and cyclohexyl vinyl ethers in presence of various catalysts. Below, we describe one experiment for each ether in presence of the most effective catalyst -2,2'-azobis[2-methylpropionitrile].

1. Butyl Vinyl Ether and Hydrogen Sulfide. Experiment 94 (conditions given in Table 1). In the fractionation 7.4 g of unchanged butyl vinyl ether was obtained and also

Fraction I b.p. 40-44° (4 mm),  $n_D^{20}$  1.4489; 4 g  
 Fraction II b.p. to 125° (3.5 mm); 0.3 g  
 Fraction III b.p. 125-127° (3.5 mm);  $n_D^{20}$  1.4559; 11 g

Fraction I corresponded in constants to 2-butoxyethanethiol, which we have previously characterized [1]. It was obtained in 23.8% yield, and its mercurichloride had m.p. 137.5-138°, undepressed by admixture of the mercurichloride of 2-butoxyethanethiol obtained previously. Fraction II corresponded in constants with bis(2-butoxyethanethiol) obtained previously. Fraction III corresponded in constants with bis(2-butoxyethyl)sulfide ( $C_4H_9OCH_2CH_2$ )<sub>2</sub>S, which we have characterized previously. It was obtained in 74.5% yield.

2. Cyclohexyl Vinyl Ether and Hydrogen Sulfide. Experiment 11 (conditions given in Table 2). The whole of the cyclohexyl vinyl ether reacted. Fractionation of the reaction mixture yielded

Fraction I b.p. 78-80° (5 mm);  $n_D^{20}$  1.4865; 5.5 g  
 Fraction II b.p. 193-195° (5 mm);  $n_D^{20}$  1.4988; 11.5 g

Fraction I was pure 2-cyclohexyloxyethanethiol, the constants of which were close to those given previously [2] for this substance; it was obtained in 28.9% yield. Fraction II was almost pure bis(2-cyclohexyloxyethyl) sulfide, and was identical in constants with the sulfide that we prepared previously [2]; it was obtained in 67.5% yield.

## SUMMARY

1. The reaction conditions required for the anomalous addition of hydrogen sulfide to aryl vinyl ethers were studied. It was shown that, while the general tendency of aryl vinyl ethers is to react more slowly than alkyl vinyl ethers, the addition of hydrogen sulfide to the former proceeds entirely in the direction contrary to that required by Markovnikov's rule.
2. A simple method is proposed for the synthesis in quantitative yield of 2-aryloxyethanethiols and bis(2-aryloxyethyl) sulfides.
3. It was shown that the most effective radical catalyst for anomalous addition of hydrogen sulfide to vinyl ethers of any structure is 2,2'-azobis[2-methylpropionitrile].

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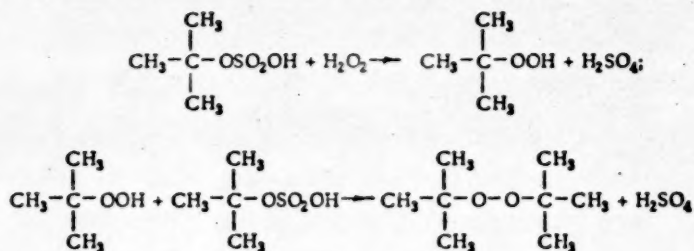
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# SYNTHESIS OF *tert*-BUTYL HYDROPEROXIDE AND *tert*-BUTYL PEROXIDE AND THEIR OPTICAL INVESTIGATION IN RELATION TO THE PROBLEM OF THE STRUCTURE OF HYDROGEN PEROXIDE

A. P. Meshcheryakov, M. I. Batuev, and A. D. Matveeva

As is well known, many peroxides are unstable compounds, which may explode violently [1]; these include, in particular, peroxides derived from dienes and acetylenic compounds. However, some very stable peroxides are known — stable not only at ordinary, but also at high temperatures. Such peroxides are those derived from tertiary alcohols, namely, *tert*-butyl alcohol and higher alcohols of this type.

In 1938 Milas and coworkers [2] prepared *tert*-butyl hydroperoxide and *tert*-butyl peroxide, which have found application, along with other peroxides, in polymerization processes [3, 4]. For the preparation of these peroxy compounds we alkylated hydrogen peroxide with *tert*-butyl hydrogen sulfate:



Whereas Milas and coworkers prepared *tert*-butyl hydrogen sulfate from *tert*-butyl alcohol, we prepared from a more accessible substance, isobutene, which can be obtained from isobutyl alcohol by dehydration over alumina at 400-420°, or from cracking gases.

## EXPERIMENTAL •

We prepared *tert*-butyl hydrogen sulfate by the absorption of isobutene in 63% sulfuric acid at 0-20°. The resulting mixture of *tert*-butyl hydrogen sulfate and sulfuric acid was transferred to a Grignard-reaction flask and was cooled to 0°. Hydrogen peroxide (27%) was then added gradually at 0-10° from a dropping funnel over a period of 30-60 minutes, the amount added being one mole for every two moles of *tert*-butyl hydrogen sulfate. Stirring was continued for 4-5 hours, and the mixture was then left at room temperature overnight. As a result of the reaction a completely transparent layer consisting of a mixture of peroxide and hydroperoxide was formed. This mixture can be used for various purposes — in particular, for polymerizations, and for the synthesis of peroxybenzoates and other peroxy compounds [2].

In order to prepare pure *tert*-butyl peroxide, free from hydroperoxide, the mixture was separated from sulfuric acid in a separating funnel and treated in the same Grignard flask at 0-10° with 10-20% NaOH solution •• which resulted in the formation of the sodium salt of the hydroperoxide and the isolation of pure (almost 100% pure) *tert* butyl peroxide, which was washed three times with small amounts of water and dried over sodium sulfate. The hydroperoxide was isolated by treating the sodium salt at 0-15° with 10% sulfuric acid, extracting the solution with ether, drying the ether solution over sodium sulfate, distilling off ether, and vacuum-distilling the residue at 35-37° (17 mm).

The total yield of peroxide and hydroperoxide was greater than 80%. When 2.1-2.2 moles of *tert*-butyl hydrogen sulfate were taken for every one mole of hydrogen peroxide, then after a long treatment (stirring for 8-10 hours) the main product was *tert*-butyl peroxide. Thus, 575 g of a mixture of 63% sulfuric acid and *tert*-butyl hydrogen sulfate (1.1 moles) reacting with 63 g of 27% hydrogen peroxide (16.81 g of H<sub>2</sub>O<sub>2</sub>) yielded 67.2 g of *tert*-butyl peroxide, which is 81.8% of the theoretically possible yield.

- Laboratory worker A. E. Korolkova took part in the experimental work.
- During the treatment with NaOH solution there was a transient purple coloration.

## Physicochemical Constants and Analytical Results

1. tert-Butyl Hydroperoxide: b.p. 35-37° (17 mm); M 90.12;  $d_4^{20}$  0.8960;  $n_D^{20}$  1.4015. The literature gives  $d_4^{20}$  0.896;  $n_D^{20}$  1.4013.

Found %: C 52.83; H 11.0; 11.03  
 $C_4H_{10}O_2$ . Calculated %: C 53.3; H 11.18

2. tert-Butyl Peroxide: b.p. 13-15° (20 mm); M 146.224  $d_4^{20}$  0.7970;  $n_D^{20}$  1.3910.

Found %: C 66.18; 66.20; H 12.45; 12.69  
 $C_4H_{14}O_2$ . Calculated %: C 65.77; H 12.40

The somewhat high carbon content of the peroxide is probably to be explained by the presence of a small amount of higher peroxides.

We investigated the Raman spectra of tert-butyl hydroperoxide and tert-butyl peroxide; the spectrum data are given below. The spectra were determined on a Soviet ISP-51 spectrograph with the medium camera.

$(CH_3)_3COOH$ .  $\Delta\nu$   $cm^{-1}$ : 221(1), 270(1), 346(4), 365(4), 413(1), 527(5), 562(0), 589(0), 609(0), 628(0), 670(0), 749(10), 790(0), 846(5), 884(10), 920(5), 1027(4), 1063(0), 1194(4), 1252(6b), 1424(0), 1454(10), 1471(2), 2655(0), 2721(1), 2884(4\*), 2931(10\*), 2987(10\*), 3236(3 band), 3320-3500(3band with maximum at 3403), 3546(1).

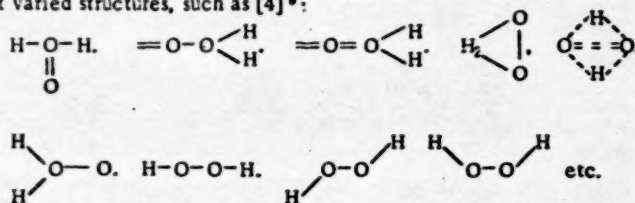
$(CH_3)_3C-O-O-C(CH_3)_3$ .  $\Delta\nu$   $cm^{-1}$ : 245(5), 263(0), 291(6), 350(2), 372(0), 513(8), 772(10), 862(10), 904(0), 926(3), 1022(3), 1041(3), 1210(3), 1241(3), 1274(4), 1426(0), 1453(9), 2712(2), 2762(0), 2882(4\*), 2930(10\*), 2986(10\*).

NOTE: b indicates a broad line; the asterisk denotes lines occurring on a background.

The Raman spectrum of tert-butyl hydroperoxide was determined also in carbon tetrachloride solution at molar concentrations of 9.6 and 4 %. In the spectrum of the first solution, in the frequency range of the hydroxyl group only the frequency  $3546\text{ cm}^{-1}$  was preserved, and weak traces of the frequency  $3622\text{ cm}^{-1}$  appeared. In the spectrum of the second solution, the intensity of the latter frequency was much higher, while the frequency  $3546\text{ cm}^{-1}$  was preserved at fairly high intensity (the ratio of the intensities of the frequencies  $3546$  and  $3622\text{ cm}^{-1}$  was 3:1).

The investigated hydroperoxide can be regarded as a derivative of hydrogen peroxide in which one of the hydrogens has been replaced by the group  $C(CH_3)_3$ . It is to be expected, therefore, that the hydroperoxide will retain some of the main optical characteristics of hydrogen peroxide.

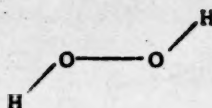
In the course of chemical and physicochemical investigations on hydrogen peroxide, this compound has been assigned the most varied structures, such as [4]\*:



Optical investigations of the last two or three decades have directly established the presence of the linkages  $-O-O-$  and  $O-H$  and the absence of the linkage  $O=O$  in the hydrogen peroxide molecule. Hence, many of the proposed structural formulas for hydrogen peroxide containing ter- and quadri-valent oxygen, etc., have automatically dropped out. The results of the optical investigation of hydrogen peroxide, taken in conjunction with the fact that its dipole moment is so high ( $2 \cdot 10^{-18}$  in dioxane and  $2.06 \cdot 10^{-18}$  in ether) and with the established absence of free rotation around the axis  $-O-O-$ , have led to the now generally accepted view of the nonplanar structure of the hydrogen peroxide molecule: the linkage  $O-H$  forms an angle of about  $110^\circ$  to the  $-O-O-$  axis, and  $H-O-O$  and  $O-O-H$  are in mutually perpendicular planes [4, 5].

\* The broken lines represent partial valencies and the arrow represents a coordinate semipolar covalent link.





Various physicochemical data indicate that hydrogen peroxide is an associated liquid, and the available Raman spectrum data [6] show directly that this association is the result of hydrogen bonding (in alcohol the hydroxyl frequency is represented not by a line, but by a band having a maximum at  $3395\text{ cm}^{-1}$ ). The degree of association at  $0^\circ$ , determined by the formula of Ramsay and Shields, has been given as 3.48 [7]. The density of hydrogen peroxide is very much greater than those of water and organic hydroperoxides [1], as can be seen from the data cited.

Peroxy compound	Temperature ( $^\circ\text{C}$ )	Density (g/cc)
$\text{H}-\text{O}-\text{O}-\text{H}$ . . . . .	22	1.4403
$\text{CH}_3-\text{O}-\text{O}-\text{H}$ . . . . .	15	0.9967
$\text{C}_2\text{H}_5-\text{O}-\text{O}-\text{H}$ . . . . .	15	0.9550
$\text{CH}_3\text{CH}_2-\text{O}-\text{O}-\text{CH}_2-\text{OH}$ . . . .	16	1.0453

This last fact indicates the particularly close packing of hydrogen peroxide molecules brought about by the action of hydrogen bonds. It is interesting to note that the addition of water sharply reduces the density of hydrogen peroxide [8]: water molecules, by forming hydrogen bonds with hydrogen peroxide molecules, break down the specific close packing with consequent reduction in the density.

Apart from the hydroxyl frequencies referred to above (band with maximum at  $3395\text{ cm}^{-1}$ ), the Raman spectrum of hydrogen peroxide contains the frequency  $887\text{ cm}^{-1}$  (vibration of O-O) and the frequency  $1421\text{ cm}^{-1}$  (deformational vibration of the linkage O-H) [5, 9].

However, in investigations on hydrogen peroxide there is an obvious underestimation of the part played by the hydrogen bond in various aggregated states of this substance.\* There is a very notable obscurity in the results of optical investigations on hydrogen peroxide, and it is essential to remove it before considering the hydroperoxide that we have investigated. Up to 1950, the same frequency was found for the hydroxyl group of hydrogen peroxide in both the liquid and gaseous ( $60^\circ$  at 18 mm) states by the infrared-absorption method, namely,  $3418\text{ cm}^{-1}$  [5, 10]. As hydrogen bonds are generally broken in the gaseous state with the formation of monomers, it was concluded [5] that in the liquid phase (as also in the gas phase) hydrogen peroxide is only weakly associated, so that individual molecules of the liquid will be characterized by the same hydroxyl frequency as the monomeric molecules of the gas phase. In view of the statements that we have made above concerning the association of hydrogen peroxide molecules by hydrogen bonding and the resulting very dense packing of molecules into associated complexes, the data cited on the identity of hydroxyl frequencies (a band with a maximum at  $3418\text{ cm}^{-1}$ ) show definitely that under these experimental conditions the frequency of the hydroxyl of hydrogen-bonded associated complexes is observed even in gaseous hydrogen peroxide. Indeed, under these experimental conditions, the frequency of the hydroxyl of isolated hydrogen peroxide molecules was not observed; it must undoubtedly lie at a higher frequency than  $3400\text{ cm}^{-1}$ . This view is supported by the following data: hydrogen peroxide has an appreciable acid dissociation constant (into  $\text{H}^+$  and  $\text{OOH}^-$ ); it has been estimated [4] at  $1.78 \cdot 10^{-12}$  (Evans) and  $1.55 \cdot 10^{-12}$  (Kargin). It is considerably higher than the dissociation constant of aliphatic alcohols (e.g. methanol,  $1 \cdot 10^{-16}$ ), but it is less than the constant for phenol ( $1.06 \cdot 10^{-10}$ ), and of course very much less than the constants of formic ( $2.1 \cdot 10^{-4}$ ) and acetic ( $1.8 \cdot 10^{-5}$ ) acids. The frequency of the hydroxyl of the monomeric hydrogen peroxide molecule should therefore be greater than in formic acid ( $3563\text{ cm}^{-1}$ ) and phenol ( $3603\text{ cm}^{-1}$ ), but less than in methanol ( $3670\text{ cm}^{-1}$ ) [12].

In this connection it must be noted that in a recent investigation reported in 1950 [13] a band at  $3590\text{ cm}^{-1}$  was observed in the infrared spectrum of gaseous hydrogen peroxide under more severe conditions ( $90^\circ$  and 15 mm) while the frequency of  $3400\text{ cm}^{-1}$ , observed earlier [5, 10] under somewhat milder conditions ( $60^\circ$  and 18 mm) in the gas phase and also in the liquid phase, could not be detected under these conditions. The author [13], without even considering the question of the association of hydrogen peroxide molecules by hydrogen bonding, of the dependence of this association on the experimental conditions, and of the effect of all these circumstances on the spectrum of the hydroxyl group, provisionally, but without any basis, assigned the frequency of  $3400\text{ cm}^{-1}$  to the symmetrical, and the frequency of  $3590\text{ cm}^{-1}$  to the antisymmetrical, vibration of the hydroxyls of the isolated hydrogen peroxide molecule. It will be evident, however, from the consideration given above that the frequency  $3400\text{ cm}^{-1}$  (which is in the form of a broad band in the Raman spectrum) can in no circumstances be assigned to the hydroxyl of the isolated hydrogen peroxide molecule. Its replacement by the frequency  $3590\text{ cm}^{-1}$  in gaseous hydrogen peroxide at a somewhat higher temperature ( $90^\circ$  instead of  $60^\circ$ ) undoubtedly indicates that under these conditions the associated complexes are broken down into simpler ones, but it is very unlikely that the frequency  $3590\text{ cm}^{-1}$  is that of the hydroxyl of the monomeric molecule; it is probable that it is the frequency of a hydroxyl forming a part of the dimer ring, which is not broken down under the experimental conditions.† the frequency of the hydroxyl of the monomeric

\* By way of example we may point out that in Pozin's monograph [4], in which a large amount of material is gathered together from the literature, there is no mention of the presence of a hydrogen bond in hydrogen peroxide; the same is true of Riche's book [1].  
 † See following page.

hydrogen peroxide molecule is still higher and has not yet been detected. Apart from the physicochemical data cited, the results of our optical investigations on tert-butyl hydroperoxide also support this view.

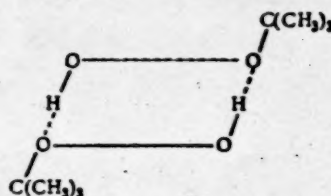
In this hydroperoxide the main features of the structure of hydrogen peroxide are retained. The frequencies observed vary only slightly from those of hydrogen peroxide: the frequency of the vibration of the O—O group is  $884\text{ cm}^{-1}$  (877 for hydrogen peroxide), the frequency of the deformational vibration of the hydroxyl group is  $1424\text{ cm}^{-1}$  (1421 for hydrogen peroxide), and there is a hydroxyl band with its maximum at  $3403\text{ cm}^{-1}$  (3395 for hydrogen peroxide), i.e., in the investigated hydroperoxide in the liquid state, association occurs by hydrogen bonding (the hydroxyl frequency is displaced toward the lower frequencies and is smeared into a band). But apart from this band, in the region of the hydroxyl frequencies there is a frequency of  $3546\text{ cm}^{-1}$ , which is preserved also in the spectra of the 9.6 % and 4 % solutions of the hydroperoxide in carbon tetrachloride, in which the other frequencies of this region disappear and a new frequency of  $3622\text{ cm}^{-1}$  makes its appearance — faintly in the spectrum of the first solution, and as a more intense line in the spectrum of the second. This is a new phenomenon, not to be found in the results given above for hydrogen peroxide. We shall explain the significance of this phenomenon.

As our cryoscopic investigations showed, the hydroperoxide is a substance that is associated by hydrogen bonding. At a 4 mole-% concentration in benzene solution the association coefficient of the hydroperoxide is 1.48, i.e., by no means all of the hydrogen-bonded associated complexes are broken down into monomer at this concentration. At a concentration in benzene solution of 8–10 mole-% there is a very definite predominance of dimer, and with increase in concentration the association coefficient increases still further.

#### Cryoscopic Determination of the Molecular Weight of tert-Butyl Hydroperoxide in Benzene

Concentration of solution (mole-%):	4	7.8	8.4	16.8	32.9
Association coefficient:	1.48	1.88	1.94	4.02	8.57

Since, unlike hydrogen peroxide, it has only one hydroxyl group, the investigated hydroperoxide forms simpler associated complexes, and its main association unit, unlike that of hydrogen peroxide with its two hydroxyls (see above), is a planar dimer ring:



tert-Butyl hydroperoxide in benzene solution at a mole percentage of 8–10 exists almost entirely in the form of this dimer ring, but at 4 mole-% part of these rings are broken with the formation of monomeric molecules. On the other hand, at higher concentrations and in the liquid state further association occurs into complexes formed from many molecules, resulting, in particular, by the further hydrogen bonding of the already existing dimer rings in layer fashion.

In the light of these considerations, the results that we have discussed relating to the optical investigation of the hydroxyl region of the spectrum are fully comprehensible. The frequency  $3546\text{ cm}^{-1}$ , which is present in the spectrum of the 9.6 and 4 mole-% solutions of the hydroperoxide in carbon tetrachloride, is to be assigned (in accordance with the cryoscopic data cited above) to the hydroxyl group of the dimer ring shown above, in which the association occurs through two hydrogen bonds. The fact that this frequency is lower than that of the hydroxyl of isolated formic and acetic acid molecules (in the gas phase [12]) provides particularly strong support for the view that under these conditions we are indeed concerned with the frequency of a hydroxyl that is taking part in a hydrogen bond, and not with the frequency of the hydroxyl in an isolated molecule. The higher frequency of  $3622\text{ cm}^{-1}$  characterizes the vibrations of the hydroxyl of monomeric molecules, which in the first solution are present only in traces (judging from the cryoscopic data), but in the second are present to the extent of about one in five of all the hydroperoxide molecules present in the solution. The presence in the liquid hydroperoxide of the frequency  $3546\text{ cm}^{-1}$  in addition to the band indicates that in the liquid state dimer rings are able to exist in appreciable amount along with the polymeric complexes.

The frequency of the hydroxyl group of the monomeric molecule of the investigated hydroperoxide is higher than the hydroxyl frequency of monomeric fatty acids (formic, etc.) and phenols, but lower than that of trimethylsilanol, methanol, and other substances, which is in accord with the discussion given above of the degree of acidity of these compounds [12, 14].

\* As is well known, complete breakdown of the hydrogen-bonded dimer ring of acetic acid occurs only at  $200^\circ$  (the boiling point of acetic acid is  $118.1^\circ$ ).

# Hydroxyl Frequency of Monomeric Molecules of Various Compounds (cm<sup>-1</sup>)

OH <sup>-</sup> ion .....	4200	Phenol .....	3603
Trimethylsilanol .....	3702	Acetic acid .....	3578
Methanol .....	3683	Formic acid .....	3563
tert-Butyl hydroperoxide .....	3620	•OH radical .....	3480

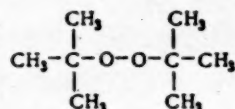
In accordance with our discussion above the frequency of the hydroxyl of the monomeric molecule of hydrogen peroxide should also be found in the Raman spectrum in the region of 3622 cm<sup>-1</sup> (symmetrical vibration) and in the infrared spectrum (antisymmetrical vibration) at a somewhat higher frequency. If we regard the frequency 3590 cm<sup>-1</sup> in the infrared absorption spectrum as the frequency of antisymmetrical vibrations of the hydroxyls of the dimer ring of hydrogen peroxide, then in the hydrogen peroxide Raman spectrum the vibration frequency of these hydroxyls (symmetrical vibration) should be somewhat lower.

Let us now turn to the question of the extent to which the optical manifestation of a quaternary carbon atom at one or other end of a carbon chain is preserved in the investigated hydroperoxide and peroxide, in which one of the C-C bonds of the quaternary carbon atom is replaced by a C-O atom.

The presence of a quaternary carbon atom at the end of the chain of a hydrocarbon molecule is characterized by a set of fairly intensive lines - 746, 926, 1207, 1250 cm<sup>-1</sup> [15]. The spectrum of the investigated hydroperoxide contains the frequencies 749, (10), 920(5), 1194(4), 1252(6b). As will be seen, the replacement of one of the C-C bonds of the quaternary atom by C-O, does not produce any essential change in the set of frequencies characteristic of this branching. In tert-butyl peroxide this set of frequencies is again largely preserved with some of them slightly higher: 772(10), 926(3), 1210(3), and the fourth split into two, 1241[3] and 1274(4). The O-O frequency in tert-butyl hydroperoxide is close to that of hydrogen peroxide (884 and 877 cm<sup>-1</sup>, respectively), and in tert-butyl peroxide it is split into two, 862 and 904 cm<sup>-1</sup>.

The high symmetry of the tert-butyl peroxide molecule, as compared with the tert-butyl hydroperoxide molecule, results in a great simplification of the spectrum (the appearance of a large number of degenerate vibrations): whereas in the Raman spectrum of tert-butyl hydroperoxide 31 vibrations were observed out of a possible 42 (for 16 atoms in the molecule), of the 78 possible vibrations of the tert-butyl peroxide molecule (18 atoms in the molecule) only 22 were observed.

Unlike other alkyl peroxides, tert-butyl peroxide has two quaternary carbon atoms in its molecule:



and it is for this reason that it is so very stable, for in its molecule the carbons adjacent to the oxygens are not attached to hydrogen and do not carry double or triple bonds, so that under ordinary conditions (room temperature) a chain oxidation reaction (which in other peroxides often occurs, leading to violent decomposition and explosions) cannot readily occur.

## SUMMARY

1. It is shown that tert-butyl hydroperoxide and tert-butyl peroxide can be prepared from isobutene.
2. It is shown that in previous investigations insufficient account has been taken of the part played by hydrogen bonding in hydrogen peroxide, of which tert-butyl hydroperoxide is a derivative (a fact that is amply confirmed by the presence in the Raman spectrum of the frequencies associated with all of the analogous vibrations of the molecules of the two substances). A study of the Raman spectrum of tert-butyl hydroperoxide shows that hydrogen bonding occurs in this substance. The optical characteristics of the hydroxyl group have been found for complexes formed from many molecules associated through hydrogen bonds (band with a maximum at 3403 cm<sup>-1</sup>), for the dimer ring (line at 3456 cm<sup>-1</sup>), and for the monomeric molecule (line at 3622 cm<sup>-1</sup>). This optical characterization was confirmed by a cryoscopic investigation. The degree of acidity of tert-butyl hydroperoxide was determined optically. It was shown that the optical characteristics of quaternary branching at the ends of the chains of tert-butyl hydroperoxide, tert-butyl peroxide, and the corresponding hydrocarbons were almost identical.



3. The stability of the investigated peroxide is explained by its structural characteristics.

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# EXCHANGE AND CLEAVAGE REACTIONS OF QUATERNARY AMMONIUM SALTS

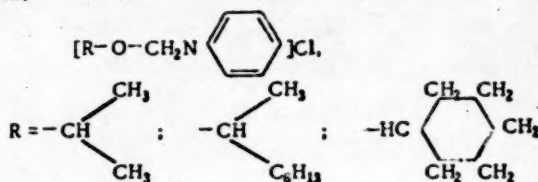
## COMMUNICATION 9. REACTION OF QUATERNARY AMMONIUM SALTS OF THE TYPE



V. N. Setkina, N. K. Baranetskaya, and D. N. Kursanov

We have shown previously [1, 2] that quaternary ammonium salts containing an alkoxymethyl group readily undergo exchange reactions in which the alkoxymethyl group changes places with the hydrogen of the hydroxyl group of a primary alcohol. The reaction has been extended to phenols [3], carboxylic acids and their salts [4], ethers [5], and esters [6]. It was of interest to determine whether the exchange reaction could be extended also to secondary and tertiary alcohols. We found no data on this in the literature. It was thought that the tendency of secondary, and particularly tertiary, alcohols to undergo dehydration might result in a change in the main direction of reaction. In our investigation of the reactions of quaternary ammonium salts with secondary and tertiary alcohols, we have used 1-(alkoxymethyl)pyridinium salts:

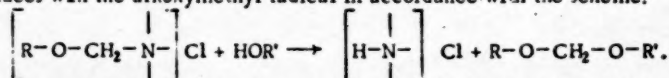
in which



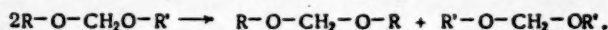
These salts were prepared by the condensation of the chloromethyl ethers of secondary alcohols with pyridine. The chloromethyl ethers were prepared by a previously described method [7-10], and the constants of our products are given in Table 1.

We were not successful in synthesizing chloromethyl ethers of tertiary alcohols, and we were unable to find evidence of the existence of such ethers in the literature.

We investigated the exchange reactions of the quaternary ammonium salts with isopropyl alcohol, sec-butyl alcohol, cyclohexanol, 2-octanol, tert-butyl alcohol, and 2-methyl-2-butanol. Equimolecular amounts of the quaternary salt and the alcohol were heated at 100-120° for 10-16 hours. It was found that the reaction products were formals, so that, as in the case of the primary alcohols, the hydroxyl hydrogen of secondary and tertiary alcohols changes places with the alkoxymethyl radical in accordance with the scheme:



When R and R' were different, then, as in the case of primary alcohols [16-18], the unsymmetrical formals underwent symmetrization, and all three possible formals were found among the reaction products:



It should be noted that the yield of formals obtained from secondary and tertiary alcohols did not exceed 50-60%, whereas primary alcohols gave formals in almost theoretical yield.

Table 2 gives the constants of formals containing tertiary and secondary radicals which we have prepared by the exchange reaction.

## EXPERIMENTAL

### Reaction of 1-(Alkoxymethyl)pyridinium Salts with Secondary and Tertiary Alcohols

The procedure used in the preparation of 1-(alkoxymethyl)pyridinium salts has been described previously [10].

TABLE 1

No.	Formula	B.p. in °C (p in mm)	$d_4^{20}$	$n_D^{20}$	Molecular refraction		Cl content (%)	
					Found	Calc'd	Found	Calc'd
1	$C_6H_{11}O-CH_2-Cl^*$	72.2 - 72.8° (12)	1.0558	1.4678	39.12	38.84	23.66	23.86
2	$\begin{array}{c} CH_3 \\ \diagdown \\ CH-O-CH_2Cl^{**} \\ \diagup \\ CH_3 \end{array}$	27.7 - 28.0 (45)	0.9742	1.4074	27.46	27.18	32.28	32.66
3	$\begin{array}{c} CH_3 \\ \diagdown \\ CH-O-CH_2Cl^{***} \\ \diagup \\ C_6H_{13} \end{array}$	98 - 99 (18)	0.9246	1.4357	50.50	50.27	19.60	19.84

\* Data in the literature: b.p. 75° (13-14 mm) [11]; b.p. 183-185°.  $d_4^{20}$  1.0712;  $d_4^{20}$  1.0432;  $n_D^{20}$  1.4713 [12].

\*\* Data in the literature: b.p. 98-100° [13]; b.p. 101-102° (760 mm);  $d_4^{20}$  0.972 [14]; b.p. 97-98°;  $d_4^{20}$  0.9790;  $n_D^{16}$  1.4592 [12]; b.p. 36° (45 mm); 101° (750 mm);  $d_4^{20}$  0.9843;  $n_D^{20}$  1.4095 [15].

\*\*\* Chloromethyl 1-methylheptyl ether is here described for the first time.

1. 1-(Cyclohexyloxymethyl)pyridinium Chloride ( $C_6H_{11}OCH_2NC_5H_5Cl$ ) and Cyclohexanol  $C_6H_{11}OH$ . A mixture of 30.64 g (0.135 mole) of 1-(cyclohexyloxymethyl) pyridinium chloride and 13.47 g (0.135 mole) of cyclohexanol was heated at 100° for six hours under reflux. The reaction mixture was cooled and treated with water, and the upper, water-insoluble layer was separated, washed several times with small amounts of water, and dried with calcium chloride. Fractionation yielded:

Fraction I, b.p. 72-140° (15 mm); 0.6 g  
 Fraction II, b.p. 140-145° (15 mm); 19.47 g  
 A very slight residue

Two further distillations of Fraction II yielded 18.0 g of a substance boiling at 135.0 - 135.5° (11 mm). Its constants and analysis (Table 2, No. 1) show that this substance was pure dicyclohexyl formal. The yield was 63.0%. Data in the literature: 279-280° (760 mm);  $d_4^{20}$  0.9716;  $n_D$  1.470; [19]; b.p. 139-140° (14 mm);  $d^{21}$  0.9741;  $n_D^{21}$  1.4702 [11].

2. 1-(1-Methylheptyloxymethyl) pyridinium Chloride ( $\begin{array}{c} CH_3 \\ \diagdown \\ CH-O-CH_2NC_5H_5Cl \\ \diagup \\ C_6H_{13} \end{array}$ ) and 2-Octanol

$CH_3-CHOH-C_6H_{13}$ . A mixture of 14.42 g (0.056 mole) of 1-(1-methylheptyloxymethyl)pyridinium chloride and 7.29 g (0.056 mole) of 2-octanol was heated at 110° for 16 hours and then treated as in the preceding experiment. Fractional distillation yielded:

Fraction I, b.p. 58-149° (8 mm); 2.39 g  
 Fraction II, b.p. 149-155° (8 mm); 7.88 g  
 A very slight residue

Further distillation of Fraction II yielded a substance (7.02 g) boiling at 152.5-153.0° (9 mm), and its molecular refraction and analysis showed that it was bis(1-methylheptyl) formal (Table 2, No. 6). The yield was 46.0%. Data in the literature: b.p. 175-177° (16 mm);  $d_4^{20}$  0.8499 [20].

3. 1-(Cyclohexyloxymethyl)pyridinium Chloride ( $C_6H_{11}OCH_2NC_5H_5Cl$ ) and sec-Butyl Alcohol  $CH_3CHOH-CH_2-CH_3$ . A mixture of 76.81 g (0.34 mole) of 1-(cyclohexyloxymethyl)pyridinium chloride and 25 g (0.34 mole) of sec-butyl alcohol was heated at 120-125° for 12 hours. The reaction products were treated as in the preceding experiments. Fractional distillation yielded:

Fraction I, b.p. 60-70° (20 mm); 11.48 g  
 Fraction II, b.p. 70-100° (20 mm); 0.93 g  
 Fraction III, b.p. 100-115° (20 mm); 22.71 g  
 Fraction IV, b.p. 115-148° (20 mm); 0.80 g  
 Fraction V, b.p. 148-152° (20 mm); 9.35 g

TABLE 2

No.	Formula of formal	B.p. in °C (p in mm)	d <sub>4</sub> <sup>20</sup>	n <sub>D</sub> <sup>20</sup>	Analysis					
					Molecular refraction		C (%)		H (%)	
					Found	Calcd	Found	Calcd	Found	Calcd
1	$\text{C}_6\text{H}_5\text{OCH}_2\text{OC}_6\text{H}_5$	135.0-135.5 (11)	0.9692	1.4703	61.15	61.12	73.67 73.64	73.53	11.48 11.43	11.40
2	$\text{CH}_3-\text{CH}-\text{O}-\text{CH}_2-\text{O}-\text{CH}-\text{CH}_3$	55.5-56.0 (81)	0.8179	1.3842	37.80	37.81	63.40 63.45	63.59	12.05 12.19	12.20
3	$\text{CH}_3-\text{CH}-\text{O}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_5$	70.0-70.5 (6)	0.9089	1.4370	49.65	49.47	69.95 70.07	69.72	11.68 11.87	11.73
4	$\text{C}_6\text{H}_5-\text{CH}-\text{O}-\text{CH}_2-\text{O}-\text{CH}-\text{CH}_3$	60.5-60.8 (17)	0.8472	1.4124	47.10	47.05	67.52 67.67	67.46	12.34 12.30	12.58
5	$\text{C}_6\text{H}_5-\text{CH}-\text{O}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_5$	99.5-101.0 (15)	0.9076	1.4402	54.10	54.08	70.43 70.64	70.85	11.93 11.73	11.91
6	$\text{CH}_3-\text{CH}-\text{O}-\text{CH}_2-\text{O}-\text{CH}-\text{CH}_3$	152.5-153.0 (9)	0.8419	1.4322	83.96	83.99	75.04 75.18	74.94	13.44 13.45	13.32
7	$\text{CH}_3-\text{C}-\text{O}-\text{CH}_2-\text{O}-\text{CH}-\text{CH}_3$	128 -129 (29)	0.8351	1.4204	65.62	65.52	72.14 72.22	72.16	13.18 13.40	13.05
8	$\text{CH}_3-\text{C}-\text{O}-\text{CH}_2-\text{O}-\text{C}-\text{CH}_3$	77.0-79.5 (96)	0.8306	1.3982	46.60	47.05	67.29 67.38	67.45	12.71 12.58	12.58
9	$\text{CH}_3-\text{C}-\text{O}-\text{CH}_2-\text{O}-\text{CH}-\text{CH}_3$	71.1-71.5 (96)	0.8223	1.3930	42.44	42.43	65.53 65.45	65.70	12.29 12.24	12.41
10	$\text{CH}_3-\text{C}-\text{O}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_5$	119.5-120.5 (23)	0.9103	1.4453	58.60	58.70	71.54 71.32	71.45	12.11 11.98	12.08

\* Formals prepared for the first time

As the result of further distillations three substances were isolated:

Substance 1, b.p. 60.5-60.8° (17 mm); 10.00 g  
 Substance 2, b.p. 99.5-101° (15 mm); 21.21 g  
 Substance 3, b.p. 144.5-145° (15 mm); 8.90 g

Substance 1 was di-sec-butyl formal (Table 2, No. 4); data in the literature: b.p. 157° (730 mm) [21]. Substance 2 was sec-butyl cyclohexyl formal (Table 2, No. 5). Substance 3 was dicyclohexyl formal having  $d_4^{20}$  0.9706;  $n_D^{20}$  1.4709; found MR 61.15, the constants found being close to those already found for this compound (Table 2, No. 1).

Under the conditions of the reaction, therefore, the initial product, sec-butyl cyclohexyl formal, underwent partial symmetrization with formation of di-sec-butyl and dicyclohexyl formal. The overall yield of formals (calculated as unsymmetrical formal) was 63.8%. Taking the total yield of formals as 100%, we obtained:

Di-sec-butyl formal	- 24.9 %
sec-Butyl cyclohexyl formal	- 52.9 %
Dicyclohexyl formal	- 22.2 %

4. 1-(Cyclohexyloxymethyl)pyridinium Chloride ( $C_6H_{11}OCH_2NC_5H_5$ )Cl and Isopropyl Alcohol  $CH_3-CHOH-CH_3$ . A mixture of 75.8 g (0.33 mole) of 1-(cyclohexyloxymethyl)pyridinium chloride and 20 g (0.33 mole) of isopropyl alcohol was heated at 100° for 18 hours. The mixture was cooled and then treated as in the preceding experiments. Fractional distillation yielded:

1) Diisopropyl formal: b.p. 55.5-56° (81 mm), 5.84 g (Table 2, No. 2). Data in the literature: b.p. 55.5-56° (81 mm); 5.84 g (Table 2, No. 2). Data in the literature: b.p. 118.5°,  $d_4^{20}$  0.831 [22]; b.p. 118° [21]; b.p. 120.5-121° (765 mm);  $d_4^{20}$  0.8181;  $n_D^{20}$  1.38413 [23].

2) Cyclohexyl isopropyl formal: b.p. 70-70.5° (6 mm), 16.56 g (Table 2, No. 3).

3) Dicyclohexyl formal: b.p. 152.5-153.0° (20 mm); 9.32 g;  $d_4^{20}$  0.9695;  $n_D^{20}$  1.4705; found MR 61.08

Found %: C 73.60; H 11.39

Calculated %: C 73.73; H 11.42

The yield of formals, calculated as unsymmetrical formal, was 55.3%. Taking the total yield of formals as 100%, we obtained 18.4% of diisopropyl formal, 52.2% of cyclohexyl isopropyl formal, and 29.4% of dicyclohexyl formal.

5. 1-(Isopropoxymethyl)pyridinium Chloride ( $i-C_3H_7OCH_2NC_5H_5$ )Cl and tert-Butyl Alcohol  $(CH_3)_3COH$ . A mixture of 72.60 g (0.39 mole) of 1-(isopropoxymethyl)pyridinium chloride and 28.67 g (0.39 mole) of tert-butyl alcohol was heated at 100° for 14 hours. The reaction products were treated as in the preceding experiments. The mixture of formals was fractionated through a 25-plate column, and the following formals were obtained:

1) Diisopropyl formal: b.p. 59-59.2° (97 mm); 11.27 g;  $d_4^{20}$  0.8183;  $n_D^{20}$  1.3848; found MR 37.84. The constants found were close to the reported values (Table 2, No. 2).

2) tert-Butyl isopropyl formal: b.p. 71.1-71.5° (96 mm), 10.65 g (Table 2, No. 9).

3) Di-tert-butyl formal: b.p. 77-79.5° (96 mm), 5.82 g (Table 2, No. 8). Data in the literature: b.p. 182-185° [24]; b.p. 50-52° (18 mm);  $d_4^{20}$  0.8260;  $n_D^{20}$  1.39904 [25]. The yield of formals, calculated as unsymmetrical formal, was 49.0%. Taking the total yield of formals as 100%, we obtained 40.6% of diisopropyl formal, 38.4% of tert-butyl isopropyl formal, and 21.0% of di-tert-butyl formal.

6. 1-(1-Methylheptyloxymethyl)pyridinium Chloride  $\begin{matrix} CH_3 \\ | \\ C_6H_{13} \end{matrix} CH-O-CH_2NC_5H_5$ )Cl and tert-Butyl Alcohol

$(CH_3)_3COH$ . A mixture of 57.70 g (0.22 mole) of 1-(1-methylheptyloxymethyl)pyridinium chloride and 16.59 g (0.22 mole) of tert-butyl alcohol was heated at 120° for 17 hours. Fractional distillation resulted in the isolation of the following substances: di-tert-butyl formal, b.p. 83-84° (99 mm), 2.31 g, the constants found being close to those already found for this compound (Table 2, No. 8); tert-butyl 1-methylheptyl formal, b.p. 128-129° (29 mm), 12.50 g (Table 2, No. 7); and bis(1-methylheptyl) formal, b.p. 183.5-184.5° (27 mm), 11.20 g,  $d_4^{20}$  0.8414;  $n_D^{20}$  1.4323; found MR 84.02, the constants found being close to those found previously (Table 2, No. 6).

The yield of formals, calculated as unsymmetrical formal, was 53.7%. Taking the total yield of formals as



100%, we obtained 8.9% of di-tert-butyl formal, 48.0% of tert-butyl 1-methylheptyl formal, and 43.1% of bis (1-methylheptyl) formal.

7. 1-(Cyclohexyloxymethyl)pyridinium Chloride ( $C_6H_{11}OCH_2NC_5H_5$ )Cl and 2-Methyl-2-butanol

$\begin{array}{l} CH_3 \\ | \\ COH-CH_2-CH_3 \\ | \\ CH_3 \end{array}$  A mixture of 61.26 g (0.27 mole) of 1-(cyclohexyloxymethyl)pyridinium chloride and 23.71 g (0.27 mole) of 2-methyl-2-butanol was heated at 110-115° for 16 hours. The reaction products were treated as in the preceding experiments. Fractional distillation resulted in the isolation of the following formals:

1) Cyclohexyl 1,1-dimethylpropyl formal, b.p. 119.5-120.5° (23 mm), 5.27 g (Table 2, No. 10).

2) Dicyclohexyl formal, b.p. 155.5-156.5° (27 mm);  $d_4^{20}$  0.9693;  $n_D^{20}$  1.4702; found MR 61.14. The constants are close to those given in Table 2, No. 1. The yield was 8.83 g.

The yield of formals, calculated as unsymmetrical formal, was 26.2%. An appreciable amount of pentene isomers was also obtained.

#### SUMMARY

1. It was shown that in the reaction of quaternary ammonium salts of the type  $(R-O-CH_2-N^+)(X^-)$  with secondary and tertiary alcohols formals are formed.

2. When the radical  $R$  of the alkoxyethyl group of the quaternary ammonium salt is the same as the radical of the alcohol, symmetrical formals are obtained, but when these radicals are different, three formals, two symmetrical and one unsymmetrical, are formed. The yield of formals was 50-60%.

3. Some of the formals have been prepared and described for the first time, namely: cyclohexyl isopropyl, sec-butyl cyclohexyl, tert-butyl 1-methylheptyl, cyclohexyl 1,1-dimethylpropyl, and tert-butyl isopropyl formals.

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# MACROMOLECULAR COMPOUNDS

## COMMUNICATION 77. DEPENDENCE OF THE PROPERTIES OF ALIPHATIC POLYAMIDES HAVING "EVEN" REPEATING UNITS ON THE STRUCTURE OF THE REPEATING UNIT

V. V. Korshak and T. M. Frunze

In a previous communication we pointed out that melting points reported in the literature for some polyamides are incorrect [1]. For example, Coffman and coworkers [2] state that the melting point of 6,8-nylon (polyhexamethylenesuberamide) is 185°, whereas in fact this polyamide melts at 225° [1].

The correct melting points, as determined by us, for some polyamides derived from 1,6-hexanediamine and dicarboxylic acids having even numbers of carbon atoms in their molecules are given in Table 1.

In this table the proportion of amide groupings in the macromolecular chain is given as a percentage of the number of methylene groups. It was found that when the dependence of the melting points of these polyamides on the proportion of amide groupings was represented graphically, the straight line shown in Fig. 1 was obtained.

This straight line is described by the following equation:

$$y = 7x + 110$$

in which  $y$  is the melting point (°C) and  $x$  is the number of amide groupings expressed as a percentage of the number of methylene groups.

By the use of this equation we have calculated the melting points of some polyamides derived from "even" diamines and "even" dicarboxylic acids, and also of polyamides derived from "even" (the term refers to the number of methylene groups)  $\omega$ -amino acids and, comparing the results with data reported in the literature [3], we have in some cases obtained good agreement between our calculated values and the values determined experimentally, as can be seen from Table 2.

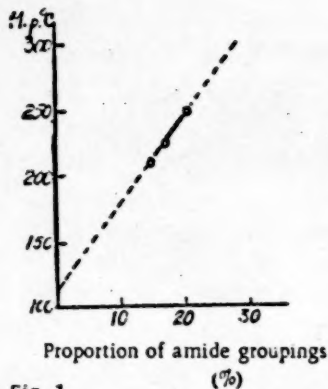


Fig. 1

TABLE 1  
Melting Points of some Polyhexamethylenealkanediamides [1]

Polyamide	Formula	M.p. (°C)	Amide/methylene ratio (mole-%)
6,6-Nylon	$[-NH(CH_2)_6NH \cdot CQ(CH_2)_4CO-]_x$	250	20.00
6,7-Nylon	$[-NH(CH_2)_6NH \cdot CQ(CH_2)_6CO-]_x$	225	16.66
6,10-Nylon	$[-NH(CH_2)_6NH \cdot CQ(CH_2)_8CO-]_x$	210	14.28

In other cases the agreement is not so good, and discrepancies of the order of 5, 10, and 15° are obtained.

On the basis of the data in Table 2, we are inclined to attribute the difference between the calculated and experimentally determined values of the melting

point to errors in the determination, possibly due to the presence of impurities, such as cresol, which lower the melting point. By the use of the equation given above it is possible to calculate the melting points of polyamides that have not yet been prepared, and also to correct melting points, when this is necessary. Results obtained in this way for polyamides derived from even diamines and even dicarboxylic acids are given in Table 3.

An interesting feature of the law that we have discovered is that the melting points of these polyamides do not depend on the way in which the methylene and amide groups are arranged in the repeating unit of the macromolecule, but depend only on the relative numbers of these groups, as can be seen from the data in Table 4, in which examples are given that illustrate this law.

TABLE 2

Calculated and Experimentally Determined Melting Points of some Polyamides

Melting point (°C)		Polyamide	Formula	Amide/methylene ratio (mole-%)
Calculated from equation	Found			
210	250	6,6-Nylon	$[-\text{NH}(\text{CH}_2)_6\text{NH}\cdot\text{CO}(\text{CH}_2)_6\text{CO}-]_x$	20.00
250	250	4,8-Nylon	$[-\text{NH}(\text{CH}_2)_4\text{NH}\cdot\text{CO}(\text{CH}_2)_8\text{CO}-]_x$	20.00
226	223	7-Nylon	$[-\text{NH}(\text{CH}_2)_7\text{CO}-]_x$	16.66
226	225	6,8-Nylon	$[-\text{NH}(\text{CH}_2)_6\text{NH}\cdot\text{CO}(\text{CH}_2)_8\text{CO}-]_x$	16.66
210	210	6,10-Nylon	$[-\text{NH}(\text{CH}_2)_6\text{NH}\cdot\text{CO}(\text{CH}_2)_{10}\text{CO}-]_x$	14.28
197	195	9-Nylon	$[-\text{NH}(\text{CH}_2)_9\text{CO}-]_x$	12.50
197	197	8,10-Nylon	$[-\text{NH}(\text{CH}_2)_8\text{NH}\cdot\text{CO}(\text{CH}_2)_{10}\text{CO}-]_x$	12.50
180	180	11-Nylon	$[-\text{NH}(\text{CH}_2)_{11}\text{CO}-]_x$	10.00
153	150	17-Nylon	$[-\text{NH}(\text{CH}_2)_{17}\text{CO}-]_x$	6.25

TABLE 3

Calculated Melting Points of some Polyamides

Diamine	Dicarboxylic acid	Melting point (°C)	
		Found	Calculated
1,4-Butanediamine	Oxalic	Not prepared	460
	Succinic	"	343
	Adipic	280	285
	Sebacic	232	226
1,6-Hexanediamine	Oxalic	Not prepared	343
	Succinic	210	285
1,8-Octanediamine	Oxalic	Not prepared	285
	Succinic	"	250
	Adipic	235	226
	Suberic	202	210
1,10-Decanediamine	Oxalic	Not prepared	250
	Succinic	"	225
	Adipic	230	210
	Suberic	Not prepared	197
	Sebacic	194	187

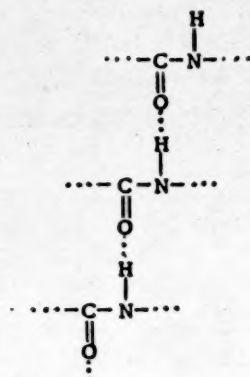
TABLE 4

Melting Points of Polyamides of Different Structure

Amide/methylene ratio (mole-%)	Polyamide	Formula	M.p.(°C)
12.50	9-Nylon	$[-\text{NH}(\text{CH}_2)_9\text{CO}-]_x$	195
	8,10-Nylon	$[-\text{NH}(\text{CH}_2)_8\text{NH}\cdot\text{CO}(\text{CH}_2)_{10}\text{CO}-]_x$	197
16.66	7-Nylon	$[-\text{NH}(\text{CH}_2)_7\text{CO}-]_x$	223
	6,8-Nylon	$[-\text{NH}(\text{CH}_2)_6\text{NH}\cdot\text{CO}(\text{CH}_2)_8\text{CO}-]_x$	225
20.00	6,6-Nylon	$[-\text{NH}(\text{CH}_2)_6\text{NH}\cdot\text{CO}(\text{CH}_2)_6\text{CO}-]_x$	250
	4,8-Nylon	$[-\text{NH}(\text{CH}_2)_4\text{NH}\cdot\text{CO}(\text{CH}_2)_8\text{CO}-]_x$	250



The amide groupings, therefore, would appear to take part in the formation of cross links between the chains of different macromolecules, thus impeding the separation of the chains and making it necessary to expend a considerable amount of thermal energy in bringing about the separation of these chains; this behavior is manifested by a rise in melting point that is proportional to the proportion of amide groupings. There can be no doubt that it is not the presence of the amide groupings, as such, that is important, but their ability to interact with one another with the formation of hydrogen bonds according to the scheme



so that a network of linkages is formed between the various macromolecules. These linkages are arranged in a plane, which is inclined at a certain angle to the axis of the macromolecule.

The good agreement between the calculated and experimentally determined proportions of amide groupings in the polyamides listed in Table 5 indicates that in these polyamides all of the amide groupings in any given macromolecule are hydrogen-bonded to amide groupings in neighboring macromolecules.

The possibility of the formation of hydrogen bonds is determined mainly by the stereochemistry of the macromolecules. Thus, in mixed polyamides, even when derived from even diamines and even carboxylic acids, not all of the amide groupings can take part in hydrogen bonding, and this fact is reflected in the melting points, as can be seen from the examples cited in Table 6. This table gives the melting points of mixed-polyamide systems that we have investigated, namely, those prepared from 1,6-hexanediamine adipate + 1,6-hexanediamine suberate (HA + HSub) and from 1,6-hexanediamine adipate + 1,6-hexanediamine sebacate (HA + HSeb).

TABLE 5

Proportions of Amide Groupings, Experimentally Determined and Calculated, in various Polyamides

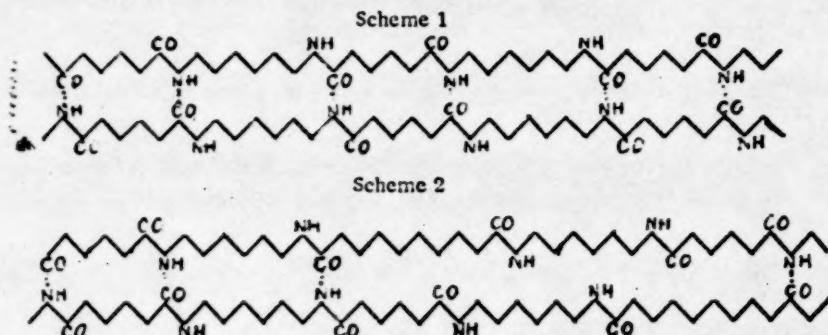
Polyamide	M.p. (°C)	Amide/methylene ratio (mole-%)	
		Determined from the melting point	Calculated from the empirical formula
17-Nylon	150	5.71	6.24
11-Nylon	180	10.00	10.00
8,10-Nylon	197	12.43	12.50
9-Nylon	195	12.14	12.50
6,10-Nylon	210	14.28	14.28
6,8-Nylon	225	16.43	16.66
7-Nylon	223	16.14	16.66
4,8-Nylon	250	20.00	20.00
6,6-Nylon	250	20.00	20.00

TABLE 6

Melting Points of Mixed Polyamides (°C)

Starting substances	Molar ratio of starting substances						
	1.0+0.0	0.8+0.2	0.6+0.4	0.5+0.5	0.4+0.6	0.2+0.8	0.0+1.0
HA + HSub	250-252	230-237	210-215	-	197-203	210-213	225-227
HA + HSeb	250-252	220-227	190-197	190-195	185-186	190-195	210-212

If, in fact, we represent diagrammatically a planar array of macromolecules of single-component polyamides derived from the salt HA (Scheme 1) (or from the salt HSch) and also of macromolecules of the mixed polyamide derived from the salts HA + HSeb (Scheme 2), then it can be readily seen that in Scheme 1 all the amide groupings can form hydrogen bonds (dotted lines), whereas in Scheme 2 not every amide grouping can form a hydrogen bond.



In considering mixed polyamides we must now distinguish between the number of amide groupings and the number of hydrogen bonds, for they are not identical, the former being always greater than the latter.

For such cases we may cast our proposed equation into a more general form:

$$y = 7z + 110$$

in which  $z = kx$ , the coefficient  $k$  being the fraction of the amide groupings that is hydrogen-bonded.

From the experimentally found melting points we may calculate the number of hydrogen bonds (per 100 methylene groups), compare it with the number of amide groupings, and determine what percentage of these groupings are free. These free amide groupings, which are not bound by hydrogen bonds, evidently play an insignificant part in determining the properties of the given polymer. In Table 7 these quantities are given for the (HA + HSeb) system of mixed polyamides already given in Table 6.

TABLE 7

Proportion of Hydrogen-bonded Amide Groupings in the System (HA + HSeb)

Molar proportions of original substances HA + HSeb	M.p.(°C)	No. of hydrogen bonds per 100 methylenes	No. of amide groupings per 100 methylenes	No. of amide groupings that are not hydrogen-bonded	
				(per 100 amide groupings)	(per 100 methylene groups)
1.0+0.0	250	20.00	20.00	0.0	0.0
0.8+0.2	220	15.71	18.52	15.17	2.81
0.6+0.4	190	11.43	17.24	33.71	5.81
0.4+0.5	190	11.43	16.66	31.40	5.23
0.4+0.6	185	10.71	16.13	33.61	5.42
0.2+0.8	190	11.43	15.15	24.56	3.72
0.0+1.0	210	14.28	14.28	0.0	0.00

The effect of stereochemical factors is particularly clear in polyamides derived from odd amino acids, diamines, and dicarboxylic acids, and this matter will form the subject of the next paper.

In conclusion we will consider some of the inferences that can be made from our proposed equation:

$$y = 7x + 110,$$

When  $x = 0, y = 110^\circ$ , so that the graph intersects the axis at the point corresponding to the melting points of polyethylene, which has a polymethylene chain free from amide groupings. When  $x = 1, y = 117^\circ$ , so that increase in the number of amide groupings by one per 100 methylene groups results in a rise in the melting point of the polyamide of  $7^\circ$ . When  $x = 100, y = 817^\circ$ , so that for 2,2-nylon (polyethyleneoxamide)  $\text{CO} \cdot \text{CO} \cdot \text{NH} (\text{CH}_2)_2 \text{NH}$ —the melting point is so high that the compound decomposes long before this temperature is reached.

On the basis of these considerations, all aliphatic straight-chain polyamides can be regarded as copolymers of ethylene ( $\text{CH}_2 = \text{CH}_2$ ) and isocyanic acid ( $\text{H}-\text{N}=\text{C}=\text{O}$ ) and in general their structure can be represented as  $(\text{CH}_2)_x (\text{CONH})_y$ . The mutual arrangement of these components has no effect on the melting point, as can be seen by a comparison of polyamides derived from  $\omega$ -amino acids with those derived from dicarboxylic acids and diamines. If the ratio  $\frac{[\text{CONH}]}{[\text{CH}_2 = \text{CH}_2]}$  is the same for two or more polyamides, then their melting points will be equal, as can be seen from Table 2.

It must be stated in conclusion that the laws that we found relating the properties (melting point, solubility, etc.) of polyamides derived from  $\omega$ -amino acids or from diamines and dicarboxylic acids with their structures, always provided that the molecules of the starting substances contain even numbers of methylene groups, present an example of simple and exact relationships that is very rare in the field of macromolecular compounds.

#### SUMMARY\*

1. The dependence of the melting point of an aliphatic polyamide on the relative numbers of amide and methylene groups in the repeating unit is examined.
2. It is shown that as the amide-methylene ratio of an aliphatic polyamide increases, there is a proportional increase in the melting point.
3. An equation is proposed which describes the dependence of the melting point of aliphatic polyamides on the amide-methylene ratio.
4. It is shown that the melting point of an aliphatic polyamide does not depend on the distribution of methylene and amide groups within the repeating unit, but only on the relative numbers of these groups.
5. The results are interpreted on the basis of the view that hydrogen bonding occurs between amide groupings.
6. It is shown that in mixed polyamides not all of the amide groupings are able to form hydrogen bonds.
7. It is suggested that aliphatic polyamides may be regarded as copolymers of ethylene and isocyanic acid.

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\* Note that this summary refers essentially to polyamides derived from components having an even number of methylene groups—Publisher.

\*\* T. p. = C. B. Translation pagination.

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## MACROMOLECULAR COMPOUNDS

### COMMUNICATION 13. DEPENDENCE OF THE PROPERTIES OF ALIPHATIC POLYAMIDES HAVING "ODD" REPEATING UNITS ON THE STRUCTURE OF THE REPEATING UNIT

V. V. Korshak and T. M. Frunze

In the preceding communication [1] we examined the dependence of the properties of polyamides having "even" repeating units on the structure of the repeating unit. It was found that there is a linear relationship between the melting point of the polyamide and the number of hydrogen bonds formed by amide groupings (relative to the number of methylene groups):

$$y = 7x + 110,$$

in which  $y$  is the melting point ( $^{\circ}\text{C}$ ) and  $x$  is the number of hydrogen bonds formed per 100 methylene groups.

With the aid of this equation we calculated the melting points of a large number of polyamides, and for many of them there was good agreement between observed and calculated values. For other polyamides, however, such agreement was not observed, and this was evidently to be explained, in the case of polyamides having even repeating units, by errors in the data given in the literature, as we succeeded in showing by our own experiments on 6,8-nylon (polyhexamethylenesuberamide), 6,9-nylon, 6,7-nylon, and other polyamides [2]. By the use of the proposed equation, we calculated melting points for known and unknown even polyamides [1].

However, an attempt to apply this equation to the large group of polyamides having odd repeating units — in which, if derived from a diamine and dicarboxylic acid, at least one of these has an odd number of methylene groups and, if derived from an amino acid, this acid has an odd number of methylene groups — was unsuccessful. In the table we cite melting points from the literature [3] and give our calculated melting points for some polyamides having odd repeating units.

A first glance at Table 1 leads us to suspect that the melting point reported for 4,13 nylon (No. 7) is too high.

The compounds may be divided into four groups according to the extent to which the amide groupings are hydrogen bonded.

The first group comprises polyamides in which about 50% of the amide groupings are hydrogen-bonded (No. 9, 11, 24).

The second group comprises polyamides in which about 75% of the amide groupings are hydrogen-bonded (No. 1, 2, 4, 8, 10, 12, 13, 14, 16, 18, 21, 25).

The third group comprises polyamides in which about 85% of the amide groupings are hydrogen-bonded (No. 3, 5, 15, 19, 22, 23).

The fourth group comprises polyamides in which more than 90% of the amide groups are hydrogen-bonded (No. 6, 7, 17, 20, 26).

Within each group there are certain resemblances between the individual compounds.

The first group includes polyamides in which both the original diamine and the original dicarboxylic acid have odd numbers of carbon atoms, which clearly corresponds to a distribution of amide groupings in which only one-half can form hydrogen bonds, as can be seen by reference to the example of 5,7-nylon (No. 9), the hydrogen bonding of which is shown diagrammatically below:

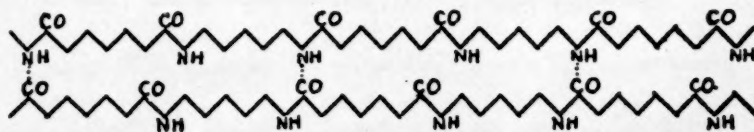
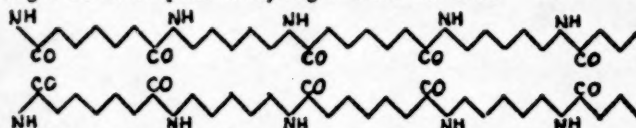


TABLE 1

Observed and Calculated Melting Points of Polyamides having Odd Repeating Units

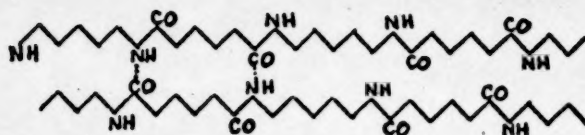
No.	Polyamide	Melting point (°C)		No. of amide groupings per 100 methylene groups	No. of hydrogen bonds per 100 methylene groups	Percentage of amide groupings that are hydrogen-bonded
		Experimentally determined	Calculated from the proportion of amide groupings			
1	$[-NH(CH_2)_5CO-]_x$	215	250	20.00	15.00	75.00
2	$[-NH(CH_2)_7CO-]_x$	178	210	14.28	9.71	68.00
3	$[-NH(CH_2)_9CO-]_x$	175	187	11.11	9.28	83.53
4	$[-NH(CH_2)_4NH\cdot CO(CH_2)_5CO-]_x$	233	265	22.22	17.57	79.07
5	$[-NH(CH_2)_6NH\cdot CO(CH_2)_7CO-]_x$	223	237	18.18	16.14	88.77
6	$[-NH(CH_2)_8NH\cdot CO(CH_2)_9CO-]_x$	209	217	15.38	14.98	92.84
7	$[-NH(CH_2)_4NH\cdot CO(CH_2)_{11}CO-]_x$	209	203	13.33	14.28	107.12
8	$[-NH(CH_2)_6NH\cdot CO(CH_2)_8CO-]_x$	223	265	22.22	16.14	72.63
9	$[-NH(CH_2)_8NH\cdot CO(CH_2)_9CO-]_x$	183	250	20.00	10.43	50.21
10	$[-NH(CH_2)_5NH\cdot CO(CH_2)_6CO-]_x$	202	237	18.18	13.14	72.27
11	$[-NH(CH_2)_7NH\cdot CO(CH_2)_7CO-]_x$	178	226	16.66	9.71	58.28
12	$[-NH(CH_2)_5NH\cdot CO(CH_2)_8CO-]_x$	195	217	15.38	12.14	78.93
13	$[-NH(CH_2)_7NH\cdot CO(CH_2)_9CO-]_x$	175	203	13.33	9.00	67.52
14	$[-NH(CH_2)_5NH\cdot CO(CH_2)_{11}CO-]_x$	176	197	12.50	9.43	75.32
15	$[-NH(CH_2)_7NH\cdot CO(CH_2)_{12}CO-]_x$	178	192	11.76	9.71	82.57
16	$[-NH(CH_2)_9NH\cdot CO(CH_2)_{14}CO-]_x$	167	183	10.52	8.14	77.37
17	$[-NH(CH_2)_5NH\cdot CO(CH_2)_{13}CO-]_x$	167	170	8.69	8.14	93.67
18	$[-NH(CH_2)_6NH\cdot CO(CH_2)_9CO-]_x$	202	237	18.18	13.14	72.27
19	$[-NH(CH_2)_8NH\cdot CO(CH_2)_7CO-]_x$	205	217	15.38	13.57	88.23
20	$[-NH(CH_2)_7NH\cdot CO(CH_2)_8CO-]_x$	226	237	18.18	16.57	91.14
21	$[-NH(CH_2)_9NH\cdot CO(CH_2)_9CO-]_x$	196	226	16.66	12.28	73.71
22	$[-NH(CH_2)_7NH\cdot CO(CH_2)_9CO-]_x$	187	203	13.33	11.00	82.52
23	$[-NH(CH_2)_9NH\cdot CO(CH_2)_8CO-]_x$	204	217	15.38	13.42	87.25
24	$[-NH(CH_2)_5NH\cdot CO(CH_2)_7CO-]_x$	163	197	12.50	7.57	49.22
25	$[-NH(CH_2)_7NH\cdot CO(CH_2)_{10}CO-]_x$	175	192	11.76	9.28	78.91
26	$[-NH(CH_2)_{10}NH\cdot CO(CH_2)_{11}CO-]_x$	172	176	9.52	8.86	93.06

A peculiarity of these macromolecules is that they are not symmetrical with respect to the axis of the molecule, since the CO and NH groups are each disposed on one side only of the molecule, so that if they have the other possible mutual arrangement in the plane no hydrogen bonds can form:



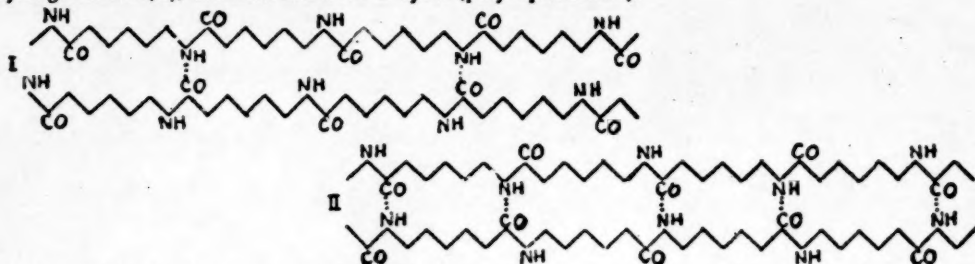
The second group includes polyamides in which one of the components—the diamine or dicarboxylic acid—has an odd number of carbon atoms, and the other component has an even number of carbon atoms. As exceptions there are some compounds in which both components are odd, their presence here being associated, possibly, with errors in the determination of the melting points or with a general tendency for the melting point to rise with increase in the length of the repeating unit. This group contains also some polyamides derived from  $\omega$ -amino acids containing odd number of methylene groups in their molecules.

The scheme of hydrogen bonding in one of the members of this group is shown below:



The hydrogen bonds in 5,6-nylon, which is shown in the diagram, alternate in pairs, but the intermediate pairs of amide groupings also form hydrogen bonds, though they are weaker owing to the greater distance of the groups with which they are linked. It would appear that two weak hydrogen bonds of this sort have the same effect as one normal hydrogen bond, so that the overall result is the same as if 75% of the amide groups formed hydrogen bonds. The possibility that this might occur was pointed out by Champetier and Aillon [4].

Polyamides derived from amino acids having an odd number of methylene groups have molecules of the vector type, i.e. the arrangement of groups differs according to the direction in which the molecule is examined - from right to left, or from left to right. The number of hydrogen bonds formed will therefore differ according as all the macromolecules are turned in the same direction or are turned alternately in different directions. In the first case only one-half of the amide groupings can form hydrogen bonds (I), whereas in the second case all can form hydrogen bonds (II), as shown below for 6-nylon (polycaprolactam):



It would appear that the first variant represents the normal arrangement of molecules (I), and the amide groupings that are more widely separated form weaker hydrogen bonds, as shown above for other polyamides of the second group.

The third group includes polyamides of the same types as those found in the second group, but the polymers of the third group are derived from starting substances having longer chains. There are no other peculiarities of structure distinguishing this group from the second. It is probable that a longer repeating unit permits the formation of a larger number of hydrogen bonds on account of the greater mobility of the macromolecule chain and the possibility of the folding of individual chains.

The fourth group includes substances derived from compounds having still longer chains, so that still more amide groupings can form hydrogen bonds. This group includes 5,20- and 10,13-nylons.

Increase in the lengths of the molecules of the original reactants, therefore, facilitates the formation of hydrogen bonds between amide groupings, and it may be expected that, when the repeating unit is sufficiently long, even polyamides derived from odd diamines and dicarboxylic acids will be able to form hydrogen bonds with the participation of all the amide groupings present, so that complete agreement will be found between the observed and calculated melting points.

#### SUMMARY

1. The relationship between the properties of polyamides having odd repeating units and the structure of their repeating units is examined.
2. It is shown that in polyamides having odd repeating units not all of the amide groupings are able to form hydrogen bonds.
3. It is shown that lengthening of the molecules of the original monomeric reactants creates more favorable conditions for the hydrogen bonding of the amide groupings of polyamides.

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• T. p. = C. B. Translation pagination.



## BRIEF COMMUNICATIONS

### CATALYTIC INERTNESS OF AMORPHOUS NICKEL IN THE HYDROGENATION OF BENZENE AND THE DEHYDROGENATION OF CYCLOHEXANE

A. M. Rubinshtein, L. Kh. Freidlin, and N. V. Borunova

While studying the effect of the conditions of calcining a mixture of nickel and aluminum hydroxides on the activity of the  $\text{Ni-Al}_2\text{O}_3$  catalyst derived from the product, we came across an interesting example of the formation of inactive nickel catalysts of amorphous structure.

A catalyst containing 30% of nickel and 70% of alumina was prepared via the aluminate from molar solutions of nickel and aluminum nitrates and 30% caustic soda solution. The washed precipitate was dried at 110-120° and then formed into a 3 x 3 mm cylinder. One series of catalysts was prepared from the above-described mixture of hydroxides by calcining separate portions for 6-12 hours at 300°, 350°, and 425° and then reducing them with electrolytic hydrogen at 350°. Another series was prepared directly from the mixture of hydroxides, which was dried at 120° and then reduced at 350°.

The activities of the catalysts were characterized by the extent to which they promoted the hydrogenation of benzene (120°; space velocity 0.3 liter per liter per hour) and the dehydrogenation of cyclohexane (300°; space velocity 0.3 liter per liter per hour). The reaction product was analyzed refractometrically.

The above-described series of catalysts were prepared several times. Usually their activities were satisfactorily reproducible and prior calcination of the original  $\text{NiO-Al}_2\text{O}_3$  mixture at 425° had no appreciable effect. In these catalyst samples the crystallinity of the two components was established by X-ray analysis.

The catalysts numbered 1 to 4 in the table, which were prepared by the same method, behaved quite differently. The table shows that catalysts prepared from a mixture of nickel and aluminum oxides calcined for 10-12 hours at 425° (No. 1, 2, and 3) or even 350° (No. 4) and then reduced with hydrogen at ordinary pressure (No. 1) or at a pressure of 500 atm (No. 2, 3, and 4) were completely inactive in the hydrogenation of benzene and the dehydrogenation of cyclohexane. The uncalcined catalysts, after reduction with hydrogen at ordinary pressure (No. 6) or at 500 atm (No. 7 and 8), were fairly active. It was clear that the difference in activity could be caused only by the difference in the pretreatment of the mixture of oxides (low-temperature drying, on the one hand, and calcination, on the other). Catalyst No. 5, which received a preliminary calcination at 300° and was reduced with hydrogen under pressure, was also active. All these catalysts gave X-ray diffraction patterns in which there was a fairly intense even background and (with the exception of catalysts No. 1 and 4) some lines of low or very low intensity corresponding to the interplanar spacings ( $d$ ) shown in the table. When these results are compared with data given in tables for Ni [1] and  $\gamma\text{-Al}_2\text{O}_3$  [2], it is readily seen that the X-ray photographs obtained from the catalysts did not give the complete diffraction pictures of Ni and  $\text{Al}_2\text{O}_3$ ; moreover, the lines were much weaker than those given by the pure substances owing to their mutual dilution in the mixture and their imperfect crystallinity. None of the lines was in the form of a doublet. Also, the lines corresponding to  $d = 1.98\text{-}2.04$  Å,  $1.75\text{-}1.77$  Å, and  $1.24$  Å could have been formed both by reflection from Ni crystals and by reflection from  $\gamma\text{-Al}_2\text{O}_3$  crystals. Some of the departures from the values of  $d$  given in tables could have resulted from defects in the crystals themselves and from high experimental errors arising from the diffuseness and low intensity of the lines obtained. When the structural data are considered together with the data on the activities of catalysts No. 1 and 4 (amorphous) and No. 2 and 3, it is found that in the last two catalysts also, the nickel was either amorphous or in the form of crystals having linear dimensions below the limit of resolution of the X-ray structure method;  $\gamma\text{-Al}_2\text{O}_3$ , on the other hand, was present in a crystalline form. In catalysts No. 5-8 each component was present partly in the amorphous and partly in the crystalline form. Before being reduced, the calcined mixture of oxides gave an amorphous photograph, which is in accord with the results of other workers [3]. It was thus shown that the catalytically inert samples were amorphous to X-rays. The amorphous nickel could have arisen during calcination by reaction between  $\text{NiO}$  and  $\text{Al}_2\text{O}_3$  with formation of the spinel  $\text{NiAl}_2\text{O}_4$ , the structure of which would be broken down in the subsequent treatment with hydrogen with the separation of nickel and alumina. Under these conditions of formation, nickel atoms are not able to associate together to form crystals of appreciable size.

TABLE

Catalyst No.	Calcination conditions		Conditions of reduction at 350°		Hydrogenation of benzene at 120° (%)	Dehydration of cyclohexane at 300° (%)	Lines on X-ray diffraction photographs of catalysts (d in Å)
	Temperature (°C)	Duration (hours)	Duration (hours)	Hydrogen pressure (atm)			
1	425	10	26	1	-	0.0	No lines present
2*	425	10	1	500	0.0	-	1.98; 1.77
3	425	10	10	500	0.2	-	2.44; 2.03; 1.75; 1.59
4	350	12	5	500	0.0	-	No lines present
5	300	6	5	500	38.4	-	1.98; 1.76
6	120	6	26	1	-	62.0	2.01
7	120	6	2	500	30.2	-	1.99; 1.50
8	120	6	5	500	96.8	61.0	2.04; 1.76; 1.60; 1.49; 1.30; 1.24

A temperature of 350-425° apparently represents a lower limit for chemical interaction between NiO and  $\text{Al}_2\text{O}_3$ , for calcination at 300° has almost no effect on the activity of the catalyst. It may be considered that the temperature at which reaction between NiO and  $\gamma\text{-Al}_2\text{O}_3$  begins is not below this level. Such a low temperature (see [3]) for the formation of a spinel is probably to be explained by the large surface of contact of the components resulting from the homogenization of the mixture of hydroxides under the influence of some factors operating during the precipitation process which we have not taken into account.

According to the multiplet theory of catalysis [4], owing to the absence of structural correspondence between the catalyst and the reacting molecule, randomly distributed nickel atoms are unable to accelerate the hydrogenation of benzene or the dehydrogenation of cyclohexane. It might be expected, however, that the hydrogenation of  $\text{aC}=\text{C}$  bond would occur on such a catalyst, i.e. that a reaction of the doublet type would occur. It was, in fact, found that, in presence of catalyst No. 4 calcined at 350° for 12 hours, 3-octene treated at 130° at a space velocity of 0.2-0.3 was hydrogenated to the extent of 67-69%. For the hydrogenation of a double bond, therefore, the catalysts containing amorphous nickel were found to be active. This may be explained by the occurrence on the surface of pairs of nickel atoms separated by a distance of about 2.49 Å, which is the distance necessary for the doublet adsorption of an olefin [5].

Our observations on this case of the formation of nickel-alumina catalysts containing amorphous nickel show that in the preparation of catalysts of this type it is necessary to avoid the formation of homogeneous systems during the precipitation of the hydroxides.

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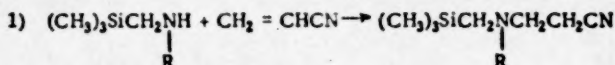
\* The sample was reduced at 400°.

# CYANOETHYLATION OF ORGANOSILICON AMINES

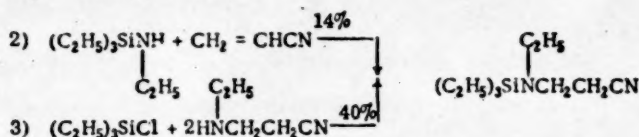
V. F. Mironov, A. D. Petrov, and N. A. Pogonkina

We have recently [1] carried out the cyanoethylation of some organosilicon alcohols in which silicon was attached to the  $\alpha$ - or  $\gamma$ -carbon.

In the present investigation we have shown that, like amines that do not contain silicon [2], organosilicon amines in which silicon is attached to the  $\alpha$ -carbon are also readily cyanoethylated:



When R was ethyl, reaction occurred readily in absence of catalysts with evolution of heat. When R was phenyl, cyanoethylation occurred only in presence of acetic acid as catalyst. On the other hand, silylamines, in which silicon is attached directly to nitrogen, behaved like the silanols and reacted with difficulty after long heating with acrylonitrile (Scheme 2):



The formation of 3-[ethyl(trimethylsilyl)amino]propionitrile by Scheme 2 was proved by a confirmatory synthesis by Scheme 3.

There is only one reference in the literature to the synthesis of the salt of a silicon-containing quaternary ammonium base, namely, the product of the action of  $\text{CH}_3\text{I}$  on  $(\text{CH}_3)_3\text{SiCH}_2\text{N}(\text{CH}_3)_2$  [3]. We have synthesized five new quaternary ammonium iodides (white crystalline powders, readily soluble in water). An attempt to prepare the same salts by the action of trialkyl(1-iodoalkyl)silanes on tertiary amines did not succeed, even under severe conditions. For example, treatment of  $(\text{C}_2\text{H}_5)_3\text{N}$  with  $\text{ICH}_2\text{Si}(\text{CH}_3)_3$  at  $200^\circ$  for ten hours gave an insignificant amount of a substance of m.p.  $256^\circ$  which did not contain silicon. Moreover, tertiary silylamines do not form silicon-containing quaternary ammonium salts with alkyl iodides. For example, when a mixture of  $(\text{C}_2\text{H}_5)_3\text{SiN}(\text{C}_2\text{H}_5)_2$  and  $\text{CH}_3\text{I}$  was allowed to stand for ten days, only a very small amount of brown precipitate formed, and this did not contain silicon.

## EXPERIMENTAL

N-[(Trimethylsilyl)methyl]ethylamine  $\text{C}_2\text{H}_5\text{HNCH}_2\text{Si}(\text{CH}_3)_3$  (I)

N,N'-Bis[(trimethylsilyl)methyl]ethylamine  $[(\text{C}_2\text{H}_5\text{N}[\text{CH}_2\text{Si}(\text{CH}_3)_3])_2]$  (II)

A mixture of 160 g of ethylamine and 150 g of (chloromethyl)trimethylsilane [4] was heated in an autoclave at about  $150^\circ$  for ten hours (with a break overnight). The contents of the autoclave were then treated with caustic soda of approximately 10% strength, and the organic layer was separated and dried with sodium sulfate. Distillation through a column having an efficiency of 15-20 theoretical plates gave 83.5 g (51%) of the amine (I), b.p.  $121.2^\circ$  (759 mm);  $n_D^{20}$  1.4155;  $d_4^{20}$  0.7594; found MR 43.33; calculated MR 43.18.

Found %: H 13.16; 13.07; C 54.79; 54.91; Si 21.31; 21.52  
 $\text{C}_6\text{H}_{17}\text{NSi}$ . Calculated %: H 13.05; C 54.89; Si 21.37;

The distillation gave also 17.7 g (15.4%) of the amine (II), b.p.  $194.5^\circ$  (760 mm);  $n_D^{20}$  1.4349;  $d_4^{20}$  0.7914; found MR 71.68; calculated MR 71.50.

Found %: H 12.45; 12.40; C 55.31; 55.15; Si 25.65; 25.88  
 $\text{C}_{10}\text{H}_{27}\text{NSi}_2$ . Calculated %: H 12.51; C 55.23; Si 25.80

The organosilicon amines (III) and (IV) were prepared under similar conditions.



N-[(Trimethylsilyl)methyl]diethylamine (C<sub>8</sub>H<sub>19</sub>)<sub>2</sub>NCH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub> (III)

A. A mixture of 91 g of diethylamine and 61.3 g of (chloromethyl)trimethylsilane was heated in an autoclave at 150° for eight hours. The product isolated was 57.6 g (72.5%) of the amine (III), b.p. 148.2° (740 mm);  $n_D^{20}$  1.4232;  $d_4^{20}$  0.7692; found MR 52.76; calculated MR 52.61.

Found %: H 13.31; 13.44; C 60.55; 60.61; Si 17.59; 17.27  
C<sub>8</sub>H<sub>19</sub>NSi. Calculated %: H 13.28; C 60.30; Si 17.61

B. A mixture of 46 g of diethylamine and 30 g of (chloromethyl)trimethylsilane was boiled for 31 hours (with breaks overnight). The precipitate was filtered off, and 7.5 g (19%) of the amine (III) was obtained. Boiling of the filtrate for a further 53 hours gave a further 5.3 g of amine, the total yield being 32.4%.

N-[(Dimethoxymethylsilyl)methyl]ethylamine C<sub>2</sub>H<sub>5</sub>NHCH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub> (IV)

A mixture of 23.2 g of ethylamine and 20 g of (chloromethyl)dimethoxymethylsilane (b.p. 139.5°) was heated in an autoclave for four hours at 150°. The contents of the autoclave were filtered from the crystalline precipitate, which was washed with dry ether. Distillation gave 5.4 g (25.6%) of the amine (IV), b.p. 156.5° (750 mm);  $n_D^{20}$  1.4118;  $d_4^{20}$  0.9120; found MR 44.52; calculated MR 44.54.

Found %: H 10.31; 10.41; C 44.16; 44.37; Si 17.11; 16.86  
C<sub>6</sub>H<sub>17</sub>NO<sub>2</sub>Si. Calculated %: H 10.50; C 44.14; Si 17.19

3-Ethyl[(trimethylsilyl)methyl]aminopropionitrile NCCH<sub>2</sub>CH<sub>2</sub>NCH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub> (V)

To 3.7 g of acrylonitrile 9.2 g of the amine (I) was added. The temperature of the mixture rose to about 40° and was kept at this level for about 15 minutes. The contents of the flask were then heated at about 60° for 12 hours. Vacuum distillation gave 10 g (77.4%) of the amino nitrile, b.p. 83.5° (3 mm);  $n_D^{20}$  1.4466;  $d_4^{20}$  0.8612; found MR 57.14; calculated MR 57.07.

Found %: H 11.04; 10.95; C 58.66; 58.66; Si 15.42; 15.45  
C<sub>9</sub>H<sub>20</sub>N<sub>2</sub>Si. Calculated %: H 10.93; C 58.64; Si 15.22

3-[N-[(Trimethylsilyl)methyl]anilino]propionitrile NCCH<sub>2</sub>CH<sub>2</sub>NCH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub> (VI)

A mixture of 3.2 g of glacial acetic acid, 10 g of acrylonitrile, and 20.6 g of N-[(trimethylsilyl)methyl]aniline [3] was heated at about 130° for 24 hours. Vacuum fractionation gave 18.3 g (68.5%) of the amino nitrile (VI), b.p. 199-201° (6 mm);  $n_D^{20}$  1.5388;  $d_4^{20}$  1.9886; found MR 73.60; calculated MR 72.01.

Found %: H 8.67; 8.60; C 67.41; 67.40; Si 12.30; 11.82  
C<sub>13</sub>H<sub>20</sub>N<sub>2</sub>Si. Calculated %: H 8.67; C 67.19; Si 12.07

3-[Ethyl(trimethylsilyl)amino]propionitrile NCCH<sub>2</sub>CH<sub>2</sub>NSi(CH<sub>3</sub>)<sub>3</sub> (VII)

A. A mixture of 10 g of acrylonitrile and 19.3 g of N,1,1,1-tetraethylsilylamine [5] was heated at 77-80° for 61 hours. Distillation gave 10.7 g of unchanged silylamine and 4 g (13.6%) of the amino nitrile (VII), b.p. 262-265° (740 mm);  $n_D^{20}$  1.4575;  $d_4^{20}$  0.8914; found MR 64.82; calculated MR 65.18.

B. Chlorotriethylsilane (65 g) was added to a stirred solution of 92.7 g of 3-ethylaminopropionitrile in 250 ml of absolute ether. On the next day the precipitate was filtered off and the filtrate was vacuum-distilled twice. The product isolated was 36.5 g (40%) of the amino nitrile (VII) b.p. 265-266° (745 mm);  $n_D^{20}$  1.4590;  $d_4^{20}$  0.8923; found MR 65.11; calculated MR 65.18.

Found %: H 11.51; 11.37; C 61.78; 61.70; Si 12.61; 12.48  
C<sub>11</sub>H<sub>24</sub>N<sub>2</sub>Si. Calculated %: H 11.39; C 62.20; Si 13.21

Diethylmethyl[(trimethylsilyl)methyl]ammonium iodide I[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>3</sub>] (VIII)

Methyl iodide (6 g) was added to a solution of 3.2 g of the amine (III) in 70 ml of absolute ether. After six days the precipitate formed was filtered off, washed with ether, and dried in a vacuum. The product was 6 g of



the substance (VIII), m.p. 118°. After three days a further 0.2 g of the substance (VIII) came down from the filtrate, i.e. the yield attained 100%.

Found %: C 36.09; 36.10; H 8.25; 8.25; Si 9.11; 9.47; I 41.92; 42.06  
 $C_9H_{14}SiNI$ . Calculated %: C 35.88; H 8.03; Si 9.31 I 42.13

In a similar way the iodides of other silicon-containing quaternary ammonium bases were obtained (see table). The analyses of these compounds for C, H, Si, and I were quite satisfactory.

TABLE

Quaternary ammonium salt	Starting substances		M.p. (°C)	No. of days	Yield (%)
	Amine	RI			
$[(CH_3)_3SiCH_2N^+(C_2H_5)_2CH_3]I^-$	(III)	$CH_3I$	118	{ 6 10	99.5 100
$[(CH_3)_3SiCH_2N^+(C_2H_5)_3]I^-$	(III)	$C_2H_5I$	170	9	100
$[(CH_3)_3SiCH_2N^+(C_2H_5)_2C_3H_5]I^-$	(III)	$C_3H_5I$	144-146	10	80
$[(CH_3)_3SiCH_2N^+(C_2H_5)CH_2CH_2CN]I^-$	(V)	$CH_3I$	190	{ 12 53 82	47 72.5 85
$\left\{ [(CH_3)_3SiCH_2N^+(CH_3)C_2H_5CH_3] \right\} I^-$	(II)	$CH_3I$	140-142	{ 4 15 45	15 93.5 96.5

#### SUMMARY

1. It is shown that it is possible to effect the cyanoethylation of organosilicon secondary amines, both those in which silicon is attached to the  $\alpha$ -carbon and those in which silicon is attached directly to nitrogen.
2. It is shown that there is a great difference in behavior between these two classes of organosilicon amines in their reactions with alkyl iodides and with acrylonitrile.

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## EFFECT OF THE STRUCTURAL FACTOR ON THE CATALYTIC DECOMPOSITION OF ALCOHOLS VARYING IN MOLECULAR WEIGHT

A. M. Rubinshtein and N. A. Pribytkova

In a previous investigation [1], in which a simple dehydrating catalyst, alumina, was used, it was observed that the decomposition of alcohols having molecules of different sizes proceeded at different rates over the same sample of catalyst, and this behavior was considered to be associated with the structural characteristics of the catalyst (dimensions of the elementary crystals and the diameters of the pores). We have investigated this phenomenon in greater detail for magnesia catalysts.

The magnesia catalysts designated as I, II, III, and IV were prepared from precipitated magnesium hydroxide obtained by the treatment of 10% magnesium nitrate solution with 10% ammonia at 0°, 20°, 60°, and 100°, respectively. Catalysts V and VI were prepared from the precipitates obtained at 20° from 1% and 50% magnesium nitrate solutions, respectively. The precipitates of hydroxide were washed until reaction for nitrate was negative, converted into tablets in the same press, dried at 110-120°, and calcined in air for six hours at 425-450°. The residual water was determined in all of the catalysts by the calcination of test samples (which were also tested for activity) at 1000° until constant weight was attained. The specific surface was determined by the adsorption of iodine from carbon tetrachloride solution, the procedure described by Zettlemyer and Walker [2] being used. The linear dimensions of the crystals were established by X-ray analysis from the half-widths of the reflections from the (002), (022), and (222) planes.

The catalytic activity of the samples was determined a) from the rate of decomposition of absolute ethyl alcohol at 435°, 450°, and 465°, the space velocity being 2.7 liters per liter per hours, and b) - for Catalysts I, V, and VI - from the rates of decomposition of absolute ethyl, n-butyl, isopentyl, and n-octyl alcohols at 450°, the space velocity being maintained constant in one series of experiments (at 2.7) and being varied so that the velocities were equimolecular in another series. The experiments were carried out in a continuous-flow system, and the weight of catalyst taken was constant. The catalyst was contained in a Vaskevich reactor [3] mounted in an electric block furnace, and the rate at which the alcohol was passed into the reactor was maintained constant by means of an automatic dispenser [4].

The liquid reaction products collected in a receiver to which a reflux condenser was attached, and the gaseous products were collected over saturated brine and analyzed for hydrogen and olefin contents (dehydrogenation and dehydration). The activity was expressed as milliliters of gaseous product (hydrogen + olefin) separating under the conditions of the experiment in unit time per gram of catalyst. The selectivity coefficient was expressed as a fraction, representing the contribution made by dehydrogenation to the overall result of the two reactions.

X-Ray structure analysis showed that the samples under investigation consisted of magnesium oxide having a constant lattice, the variations from preparation to preparation being within the limits of experimental error. The mean linear dimensions of the crystals did not vary greatly among the samples (Table 1). Calcination at 1000° generally resulted in an increase by a factor of 1.3-1.5 in the mean linear dimension of the crystals. Over the temperature range investigated, and also from sample to sample, the selectivity varied very little. The fact that catalysts calcined at 1000° had greater selectivity coefficients indicates that the removal of water from the catalysts alters the ratio of the rates of dehydrogenation and dehydration in favor of dehydrogenation. The 50% reduction in the overall activity after calcination at 1000° is evidently the result of sintering and reduction in surface, which amounted to as much as 75-80% when constant weight was attained.

Experiments with alcohols containing different numbers of carbon atoms in their molecules showed (Table 2) that not only the activity, but also the selectivity, is dependent on the size of the alcohol molecule. Both at space velocities of 2.7 (Table 2, A) and at equimolecular rates (Table 2, B), there is an appreciable variation in overall specific activity, which for equimolecular rates is particularly marked as we pass from ethyl alcohol to butyl alcohol; this may result from the differences in effective specific surface [1] between one alcohol and another: some of the pores, which are accessible to the small ethyl alcohol molecule, are excluded from the process when the larger molecules of butyl and higher alcohols are reacting. The change in the selectivity of the catalysts with increase in the size of the alcohol molecule cannot, however, be explained by a change in the

TABLE 1

Catalyst No.	Residual Water (%)	Specific surface (sq.m/g)	Linear dimension of MgO crystals (A)	Activity*	Selectivity coefficient
I	2.15	104(27)	66(103)	42.9	0.77
				79.0	0.74
				<u>91.0</u> (32.7)	<u>0.74</u> (0.86)
				52.3	0.77
II	3.25	132(29)	51(83)	82.6	0.72
				<u>107.6</u> (24.9)	<u>0.70</u> (0.83)
				42.8	0.75
				64.3	0.72
III	3.50	131	57	99.7	0.72
				34.8	0.78
				61.7	0.77
				<u>—</u> (27.0)	<u>—</u> (0.84)
IV	2.95	132(33)	59(83)	87.3	0.74
				30.3	0.76
				61.3	0.72
				<u>—</u> (37.6)	<u>—</u> (0.86)
V	2.64	111(32)	59(70)	84.4	0.70
				23.2	0.76
				44.8	0.73
				<u>—</u> (31.7)	<u>—</u> (0.83)
VI	2.04	63(36)	82(80)	80.6	0.75

\* At 435°, 450°, and 465°, the results obtained at 450° being underlined. The results given in parentheses are for samples calcined at 1000°.

TABLE 2

Catalyst No.	Ethyl alcohol		Butyl alcohol		Isopentyl alcohol		Octyl alcohol	
	Activity	Selectivity coefficient	Activity	Selectivity coefficient	Activity	Selectivity coefficient	Activity	Selectivity coefficient
A. Space velocity 2.7 liters per liter per hour; 450°								
I	79.0	0.74	57.2	0.87	40.3	0.94	40.3	0.89
V	60.6	0.71	52.0	0.92	40.2	0.93	43.5	0.87
VI	42.8	0.73	37.2	0.9	17.9	0.94	28.4	0.86
B. Equimolecular rates (space velocities of 2.7, 4.6, 5.4, and 8.1 liters per liter per hour, respectively); 450°								
I	79.0	0.74	27.3	0.96	26.9	0.95	27.0	0.93
V	60.6	0.71	41.7	0.95	30.3	0.95	29.6	0.92
VI	42.8	0.73	15.9	0.94	—	—	15.6	0.94

effective specific surface. Here the operating factor is a structural one: a screening of part of the active centers as the dimensions of the molecules being adsorbed are increased. According to the multiplet theory [5] it is one of the ways in which a "framed" radical affects a process. Since the adsorbed group  $\text{CH}_2\text{OH}$  of the alcohol molecule is at a large angle to the catalyst surface in dehydrogenation, whereas the adsorbed group  $\text{CH}_2-\text{CH}_2\text{OH}$  is at a small angle in dehydration, the screening effect should show itself as a very much greater reduction in activity in dehydration reactions with increase in the size of the alcohol molecule, as compared with the reduction in activity in dehydrogenation reactions. It is in fact found that, as we pass from ethyl alcohol to butyl-alcohol, dehydration activity is reduced 7-20 fold (Table 2,B), but hydrogenation activity only twofold. This results in an increase in the selectivity coefficient. If we take the doublet adsorption scheme [5] as the basis for our considerations and take the C-C distance in alcohols to be 1.54 Å with tetrahedral valency angles [6], it can be readily shown that the ethyl alcohol molecule should fit on a magnesium oxide surface ( $d=2.40$  Å) in



the position required by the dehydration scheme with preservation of valency angles without screening of the surface and without overlapping (Data for the calculations are given in [7]). For butyl alcohol however, and still more for higher alcohols, some screening of the surface is inevitable, and the occurrence of such screening provides the explanation of the observed increase in the selectivity coefficient.

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OF THE POLYCONDENSATION OF ESTERS OF  $\alpha$ -AMINO ACIDS

K. T. Poroshin, T. D. Kozarenko, and Yu. I. Khurgin

It is known that the polycondensation of esters of  $\alpha$ -amino acids goes in two directions: 1) the formation of linear polypeptides, and 2) the formation of cyclic dipeptides, i.e. 2,5-piperazinediones (diketopiperazines):

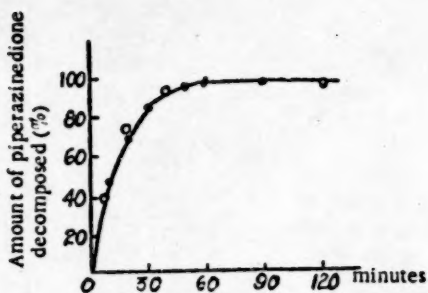
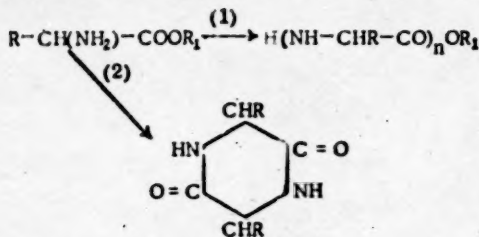


Fig. 1. Curve for the hydrolysis of 2,5-piperazinedione in 0.1 N NaOH at 40°: O) titration with copper; O) from the reduction in amine nitrogen (van Slyke)

No accessible and sufficiently accurate methods have been reported for the determination of cyclic and linear forms in the products of the polycondensation of esters  $\alpha$ -amino acids.

Determination of the cyclic forms by Gavrilov and Balabukha's ionophoresis method [1] gives satisfactory results, but is associated with great experimental difficulties. Moreover, ionophoresis can be applied only to water-soluble polycondensation products. The method of sublimation [2, 3] from the mixture of piperazinediones and polypeptides in a vacuum at high temperature ( $10^{-3}$  mm;  $140-150^{\circ}$ ) has an important defect in that part of the peptides undergo thermal degradation under these conditions with formation of a certain amount of piperazinediones [2].

When entering upon a study of the mechanism of the polycondensation of esters of  $\alpha$ -amino acids, we were faced with the necessity of developing a simpler and sufficiently accurate method for the quantitative estimation of cyclic forms. We decided to examine a method based on the known action of alkali on piperazinediones, which are broken down with formation of dipeptides [4].

The absence of free amino acids among the substances formed in the earlier stages of the degradation of piperazinediones may be associated with nonequivalence of the peptide linkages in this compound. We studied the degradation of piperazinedione under various conditions of alkali concentration and temperature, and on the basis of this work we found the optimum conditions for complete degradation. The quantitative yield of dipeptides in the polycondensation products was determined after destruction of the piperazinediones from the increase in amine nitrogen (van Slyke) and also from the amount of bound copper in the "biuret" dipeptide copper complex ( $\lambda_{\max}=610 \text{ m}\mu$ ). One of us [5] has shown previously by the method of differential spectrophotometry that the formation of copper complexes in a polypeptide mixture occurs in a definite sequence. As copper is added, at first the complexes of tetrapeptides and still longer polypeptides are formed ( $\lambda_{\max}=510\text{--}515 \text{ m}\mu$ ). The complexes of the tripeptides ( $\lambda_{\max}=580 \text{ m}\mu$ ) are formed after the complexing of the longer peptides is complete. Finally, the blue dipeptide complexes are formed. An analogous sequence for the binding of copper by the glycine peptides was found by Dobbie and Kermack [6] on the basis of potentiometric and spectrophotometric data. On the basis of these considerations we developed a method of visual titration of the amount of dipeptides bound to copper. The initial point of the titration was the point at which the formation of "red" (tetrapeptide) and "violet" (tripeptide) complexes ceased, and the end point was indicated by the formation of a very fine suspension of copper hydroxide.

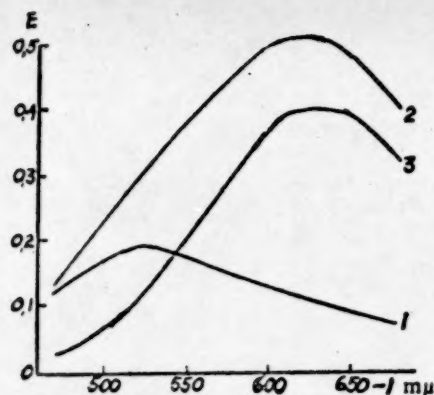


Fig. 2 Absorption spectra of the copper complexes of polycondensation products obtained from the ethyl ester of DL-alanine: 1) at transition point; 2) after the completion of complex formation; 3) absorption spectrum of copper complexes formed after the transition point.

A parallel determination by the increase in amine nitrogen gave a piperazinedione content of 8.8%. Similar piperazinedione determinations on polycondensation products obtained from the ethyl ester of DL-alanine gave  $62.8 \pm 0.2\%$  by the copper method and 59.8% by the van Slyke method. The piperazinedione content of the polycondensation products obtained from the ethyl ester of DL-alanine has been previously determined [7] by the ionophoretic method, which is possible on account of the good solubility of these products, and a value of 68% was found.

Distillation at  $140^\circ$  and  $10^{-3}$  mm gave a value of 70% for the content of piperazinedione. This value may be too high owing to the thermal degradation of linear polymers with formation of cyclic dimers. In ionophoresis, on the other hand, complete separation did not occur, since a part of the polymers did not pass to the cathode.

In order to check the accuracy of the determination of the transition point in the copper titration, the absorption spectra of copper "biuret" complexes were determined for the polycondensation products obtained from the ester of DL-alanine (Fig. 2). Curve 1 was determined at the "transition point", and the position of the maximum ( $\lambda_{\max} = 530 \text{ m}\mu$ ) corresponds to the copper complexes of tetrapeptides and still higher polypeptides. The form of the curve at wavelengths of greater than  $550 \text{ m}\mu$  indicates that a small amount of tripeptides may be present. The absorption spectrum of the copper complexes formed after the transition point (Curve 3), i.e. the differences in optical density measured after the completion of complex formation (Curve 2, and at the transition point, corresponds to the absorption due to the copper complexes of dipeptides ( $\lambda_{\max} = 620 \text{ m}\mu$ ). This confirms that in the titration with copper salt the transition point can be determined visually with sufficient accuracy.

It must be pointed out that the titration of dipeptides with a copper salt is difficult when an appreciable amount of tripeptides is present, because the colors given by di- and tri-peptides are visually similar. However, this difficulty can be removed by the use of spectrophotometric titration.

#### SUMMARY

1. A new method is proposed for the quantitative determination of piperazinediones in presence of peptides from the amount of dipeptides formed by alkaline hydrolysis. Titration with a copper salt and measurement of the increase in amine nitrogen give agreeing results.

2. The piperazinedione contents of the polycondensation products obtained from the ethyl ester of glycine and from the ethyl ester of DL-alanine are determined, the values obtained being 10% and 61%, respectively.

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## CURRENT EVENTS

### GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE USSR

At a session of a general meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR, which was held under the chairmanship of Academician M. M. Dubinin on March 30 and 31, 1955, papers were read by Academician A. A. Balandin on "The Present State of the Catalysis Problem and the Theoretical Basis of the Search for Catalysts" \*, by Corr. Memb. Acad. Sci. USSR A. D. Petrov on "The Synthesis of Branched Aliphatic Hydrocarbons via 2-Alkenyl Halides" \*\*, and by Corr. Memb. Acad. Sci. USSR A. P. Terentyev on "A New Nomenclature for Condensed Organic Systems".

Opening the discussion on the first paper, Academician M. M. Dubinin emphasized the need to consider the possible directions that future theoretical and experimental investigations may take and to indicate which of these it is most desirable to follow.

In the further discussion on this paper, Ya. T. Eidus, Doc. Chem. Sci. (Institute of Organic Chemistry of the USSR Academy of Sciences), pointed out the relationship existing between the practical problem of the rational, scientific selection of catalysts and the level reached by the theory of catalysis. Eidus considers that, owing to its sound and wide physicochemical basis, the multiplet theory forms a unifying center in which the concepts at the basis of other theories of heterogeneous catalysis are reflected in some degree or other. Thus an example of the relationship between the multiplet theory, the supersaturation theory, and Taylor's nonuniform-surface theory is revealed when we consider the effect of the micro-roughness of a catalyst surface on its activity.

The theory of active assemblages, which identifies the active sites of the catalyst with an amorphous phase, ascribes the activity to a group of atoms — the active assemblage — which corresponds in some measure to a multiplet.

The relationship between the multiplet theory and the intermediate-compound theory finds expression in the nature of the intermediate multiplet complex, in which the basic idea of the intermediate-compound theory is contained. As regards Polanyi's theory, which appeared shortly after the multiplet theory, it is extremely close to the latter and is identical with it in its basic ideas. The multiplet theory is closely related also with the theory of activated adsorption.

Of particular importance is the establishment of a relationship between the multiplet theory and the theory of the transition state. The common feature, fundamental for this relationship, is the assumption of the existence of intermediate states, described as multiplet or activated complexes; the models representing these are often identical, as in both cases configurations formed by two or more atoms of the catalyst are active.

These relationships between various theories and the multiplet theory, the alpha and omega of which is the concept of geometric and energetic correspondence between the reacting species and the catalyst, create, according to A. A. Balandin, the possibility of unifying most of the existing theories into a single one — continued Ya. T. Eidus — and the various views will find their definite places in it. In fact, the specificity of the individual theories arises from the fact that they make different approaches to the same phenomenon, so that they can supplement one another. However, difficulties arise in the unification of theories when the specificity results from the fact that the given theory specializes on phenomena from different fields of catalysis.

Ya. T. Eidus considered some forms of catalysis that occupy an intermediate place between heterogeneous and homogeneous catalysis. Some of these forms of catalysis are well known, for example the hetero-homogeneous reactions such as that of Polyakov, Semenov, and Kovalsky, in which the active center, which is formed at the surface, may be thrown out into the space, where it may initiate a homogeneous reaction; another example is

\* A. A. Balandin's paper is to be found on p. 557 of this translation.

\*\* A. D. Petrov's paper is to be found on p. 571 of this translation.

afforded by the homogeneous reactions occurring in liquid films on the surface of a heterogeneous catalyst (Semenov, Chirkov, and Goldansky).

Ya. T. Eidus stated that he had recently turned his attention to a catalytic phenomenon in which one of the main requirements of the multiplet theory — the activation of all of the original reaction components by the catalyst — was not met, activation by the catalyst surface being confined, for example, to only one of two components. This interesting phenomenon was observed in the iso-synthesis reaction and consisted in the hydrogenation of carbon monoxide with hydrogen over catalysts that were unable to activate hydrogen for example the classical dehydration catalysts, such as alumina and thoria. As the result of such "semicontact" hydrogenation at high temperatures and pressures, branched hydrocarbons are formed. In Eidus's opinion, a reaction mechanism of this sort is unique and does not correspond to true heterogeneous catalysis; it can be regarded as a special case of heterogeneous catalysis in the sense that in its mechanics rest is not regarded as the opposite of movement, but as a special case of movement characterized by zero velocity. This semicontact mechanism is a special case of a multiplet reaction in which the adsorptions are zero.

Ya. T. Eidus expressed the hope that the theory would reveal the characteristics of such examples of semicontact catalysis, since this may be of significance in the development of the principles underlying the scientific selection of catalysts. A theoretical examination of reactions proceeded by a semicontact mechanism indicates that they should be characterized by activation energies higher than those to be expected if true contact catalysis occurred. The same conclusion was reached also by Eyring.

In conclusion, Ya. T. Eidus pointed out that great progress had been made recently in the prediction of the selectivity of a given catalyst in the reactions of functional groups, but the finer points — promoting and activation, sensitivity to slight changes in the method of preparing catalysts, and others — have not yet found their rightful places in the theory of the scientific selection of catalysts.

In joining the discussion, M. I. Temkin (L. Ya. Karpov Physicochemical Institute) remarked that A. A. Balandin was the first to raise, in its general form, the question of the so-called energetic correspondence in catalysis, i.e. the question of how it is possible to select a catalyst for a given reaction on the basis of the values of the energies of the bonds formed by atoms with the catalyst. This is undoubtedly a very interesting question, for although data on bond energies are at present inadequate, they may be obtained in the future, and if it should be possible to select catalysts on the basis of these data, work on catalysis would be greatly assisted.

At a first glance it would appear — continued M. I. Temkin — that it would be impossible to do this, because reaction rates cannot be expressed unequivocally by quantities of a thermodynamical nature, such as bond energies. It is known, however, that there is a definite type of correspondence between kinetic and energetic quantities, an example of which is provided by the well known relationships in the field of acid catalysis. In principle, this justifies the posing of this question.

In addition to kinetic methods of determining the energies of bonds between atoms and the surface, it is possible to find methods that are more direct. In the Chemical Kinetics Laboratory of the Karpov Institute the study of chemical equilibria has been recently applied for this purpose, the participants in these equilibria being gaseous components, on the one hand, and surface compounds, on the other.

The equilibrium data — stated M. I. Temkin — enable the bond energies to be determined for the surface compounds. N. V. Kulkova has investigated the energies of the bonds formed by oxygen with the surfaces of various kinds of oxidative catalysts. The results of such measurements can be used for the experimental elucidation of the problem of energetic correspondence.

From the theoretical point of view it is possible to approach this problem in a way that is somewhat different from that adopted in A. A. Balandin's work, that is to say we can examine in a fairly general way the problem of a heterogeneous catalytic process composed of two stages (in general, apparently, every catalytic process must consist of stages, so that two is the least possible number). If we write down the equation for the rate of the process that corresponds to stationary-state conditions, and then, in determining the rate constants for each stage, assume the same relationship between kinetic and thermodynamical characteristics as that found for acid catalysis, we may solve the question, in its general form, of which catalyst will give the maximum reaction rate. M. I. Temkin has carried out such a treatment on the assumption that the change in activation energy from one catalyst to another is one-half of the change in the bond energy in the intermediate surface compound (this is in accord with the results that he obtained in experimental studies of the synthesis of ammonia and other reactions). It is then found that maximum reaction rate is attained when one-half of the surface is covered with the intermediate compound. Temkin distinguishes two cases. In the first, one stage attains equilibrium before the reaction as a whole



does. This occurs, for example, in the synthesis of ammonia. The required half coverage can then be expressed in terms of the thermodynamical characteristics of the equilibrium stage. In this way the problem is completely solved.

In the second case, which corresponds to that examined by A. A. Balandin, the reaction occurs under conditions far removed from equilibrium. By the approach that we have made it is now impossible to express, in a general form, the conditions for half coverage in terms of bond energies. This can be done, however, if it is assumed that the relationship between equilibrium and rate constants is valid not only for each stage separately, but also for the two stages in association. This assumption is rational when the first and second stages are analogous processes, as occurs, for example, in the doublet scheme applied by A. A. Balandin. Such reactions can be termed symmetrical. The most symmetrical reactions in this sense are isotope-exchange reactions. For the case considered by Balandin the same result is obtained by this method as that obtained by him with the aid of volcanolike curves: it is found that the sum of the energies of the bonds formed with the surface should be equal to one-half of the sum of the energies of the bonds that were broken and of the bonds that are formed.

In conclusion, M. I. Tamkin said that, although it is impossible to select the optimum catalyst on the basis of bond energies in the general case, it can be done (if the above assumptions are valid) in two important special cases: reactions in the vicinity of equilibrium, and symmetrical reactions.

In entering the discussion on the paper, Corr. Memb. Acad. Sci. USSR S. Z. Roginsky pointed out that this concentration of effort on working out the scientific principles of the selection of catalysts was very timely, but rapid progress must not be expected, for the problem is a very difficult one which has not been even partially solved, neither here nor abroad. At the same time, the theory of the selection of catalysts has given rise to some interesting concepts, and the experimental material that has been accumulated gives us reason to hope for success if we make a serious collective effort over a long period. In his paper A. A. Balandin correctly emphasized — stated S. Z. Roginsky — that the model concepts of his selection theory and the equations to which they give rise, although they apply to an extensive range of reactions, are not by any means universal and must be applied to definite types of reactions. Roginsky pointed out further that in his own investigations it had been shown that some markedly different types of catalysis mechanism existed. This fact must be taken into account in the development of a selection theory, since the laws are different for different types. For heterogeneous catalysis it has been shown that there are a few basic kinds of activation effect produced by the catalyst on the reaction. In organic catalysis one of the most common of these is acid-base activation. A solid catalyst very often acts as a solid acid and base by the same mechanism of proton transfer as that found in liquid acids and bases (and also, much more rarely, in aprotic acids). The use of solid surfaces as acid-base catalysts introduces some essentially new features.

On the surface there may exist simultaneously, and as immediate neighbors, sites having acidic and basic properties. S. Z. Roginsky pointed out that acids and bases may be obtained which surpass in strength the strongest acids and bases met in homogeneous media, that centers differing in acidity and basicity may be found on the surface and different geometric dispositions of these centers may occur, and that both the arrangement of the centers and their acid and basic properties may vary over a wide range for different catalysts, in presence of various additives, and for different methods of preparing the catalyst.

Catalysts act — continued S. Z. Roginsky — by a second type of mechanism based on electron transitions, which is just as common, but has no exact analogs in homogeneous catalysis. Whereas in acid-base catalysis the catalyst generally initiates the process by removing a proton from a substrate molecule or transferring a proton to it, in oxidation-reduction or electronic catalysis the typical initiating act of activation is the transfer of an electron to the substrate or the drawing of an electron from the substrate into the solid. Other types of catalytic action also exist.

In Roginsky's opinion it is very important to distinguish clearly the most common fundamental types of primary process of substrate activation by the catalyst, establish definite gradations and sequences among these with respect to the forces of interaction between the catalyst and the substrate, and then control this interaction in order to obtain the desired effect.

In the field of selection theory — said S. Z. Roginsky — we are already in a position to predict which catalysts will be active for the acceleration of processes of low specificity. But an extremely difficult and important problem remains — a rational approach to the selection of specific catalysts. A. A. Balandin's paper shows that a successful approach to the solution of this problem can be made on the basis of the theory of multiplets. The application of electronic concepts hold out great promise in this field. An important part should be played in the discovery

of the laws of selection by the periodic system of elements, for, in particular, the acid-base and electronic properties of substances, of which we have already spoken, i.e. the power of acting as acceptors and donors of protons and electrons, vary with changes in the elementary composition of the compounds. Basic properties become more pronounced as the atomic weight is increased and as we move from right to left in Mendeleev's periodic table; acidic properties behave similarly as we move from left to right. For a given element basic character increases as the valency falls. In the electronic properties a determining part is played by the presence of unoccupied places in the  $d$  electron shells and the number of such places. The first simple relationships for the effect of the combination of elements on their electronic properties, etc., have been found. S. Z. Roginsky considers that, if our approach to the periodic system is sufficiently profound and we make investigations under comparable conditions, the system will provide very rich and valuable material in this field, the obtaining of which is of special importance in that a large number of "blank places" remain in the periodic system with respect to the study of the catalytic properties of the elements and their compounds.

It is necessary also to take into account the possibility of exerting an extremely close control over the catalytic properties of a solid by making small additions of a definite type.

As an example, Roginsky cited the semiconductor catalyst, nickelous oxide. If 0.05-0.1% of lithium oxide is introduced into the nickelous oxide lattice (it goes into solid solution), the catalytic properties are greatly changed; in particular, the activation energy changes. The introduction of lithium increases the number of electron holes in the lattice, and this had a detrimental effect on the catalytic properties. On the other hand, the introduction of large amounts of magnesium oxide into the lattice, where it forms a solid solution, has almost no effect on the activity; here the cation has the same charge as  $Ni^{++}$  and is not able to change its charge. According to the literature, the introduction of small amounts of iron, indium, chromium, and some other trivalent elements greatly affects the conductivity, and also greatly alters the catalytic functions, their effects being in the opposite direction to that of lithium. The activity can therefore be controlled within wide limits in a rational fashion.

When a solid acts as a catalyst of the acid-base type, activation can be effected by other additions, which in combination with the catalyst give acids or bases of enhanced strength.

We stand — stated S. Z. Roginsky — at the very beginning of a great collective task — the search for scientific principles that can form the basis of the selection of catalysts. Important scientific forces have been mobilized for the solution of this problem and the creative efforts of a number of scientific teams have been concentrated on it, and this action must be regarded as correct and rational. There is reason to hope that in a few years there will be a substantial increase in the amount of reliable experimental material, accompanied by the discovery of new catalysts and considerable progress in work on the search for the scientific principles of the selection of catalysts.

G. K. Borekov, Doc. Chem. Sci. (Karpov Physicochemical Institute), pointed out that with respect to a limited number of reactions the solution of the problem would greatly contribute to the progress of the chemical industry. This problem was an extremely difficult one, however, and the gap between the requirements of practice and the possibilities of theory were very great indeed.

For cases in which the reacting substances and the catalyst form a single active complex, A. A. Balandin has shown by his multiplet theory that by evaluating the energy of formation of this complex and considering its further transformations we may predict the activation energy for the chemical reaction in presence of the given catalyst.

It should be noted, however — stated G. K. Borekov — that quantitative calculations, even approximate ones, come up against considerable difficulties. The least reliable calculation is that of the energies of the bonds formed by individual atoms of the reactants with the catalyst. It is difficult to understand how it is possible to evaluate these bond energies from energies of formation of the corresponding compounds in a phase.

If I have understood A. A. Balandin correctly — said G. K. Borekov — then in the table in which data are given for various catalysts the energies of the bonds formed with the catalysts were calculated from the experimentally determined activation energies for the dehydrogenation of hydrocarbons and the dehydration and dehydrogenation of alcohols. Though it may be possible to understand that for the dehydrogenation of hydrocarbons we may determine the energy of the bond formed by hydrogen with the catalyst, it is very difficult to imagine how the energy of the bond formed by oxygen with the catalyst can be determined for the dehydration of an alcohol. In Borekov's opinion, this last quantity has no direct bearing on the dehydration reaction, and the approximations that have to be made in the proposed scheme of calculation make it difficult to apply it in the solution of practical problems associated with the selection of catalysts. Results of greater reliability can be expected from the application of the theory to the estimation of the relative rates of various reactions over a given catalyst, as given in the paper.

G. K. Borekov discussed briefly the aspects of the problem (the scientific principles of the selection of catalysts) that were being examined in the Technical Catalysis Laboratory of the Karpov Institute on the basis of the view that the action of solid catalysts is determined by intermediate surface chemical interaction between the reactants and the catalyst.

Previous work by G. K. Borekov has shown that the activity per unit area of catalyst (specific catalytic activity) for various metal and oxide catalysts is approximately constant.

Hence, the main factor determining specific catalytic activity is the chemical composition. This fact determines the problems which, in Borekov's opinion, will have to be solved in order to create a theory of catalyst selection.

The first, immediate problem is the discovery of the general laws relating specific catalytic activity with the chemical composition of the catalyst and, as S. Z. Roginsky had pointed out, the search for these laws is best carried out with the aid of Mendeleev's periodic law, which provides the most complete generalization of chemical properties.

Working in this direction, G. K. Borekov has obtained some results on the specific catalytic activity of metals in oxidation, hydrogenation, isotope-exchange, and other reactions. It was found that, for reactions in which the activation of hydrogen occurred, the specific catalytic activities of metals in given periods of Mendeleev's system increased at first, attained a maximum when the  $d$  zone was almost filled with electrons, i.e. for Ni, Pd, and Pt, and then fell sharply to the succeeding metals of group I B. On the other hand, for the synthesis of ammonia, which is associated with the activation of molecular nitrogen, maximum specific activity was found for Fe, Ru, and Os, i.e. corresponded to the greatest deficiency of electrons in the  $d$  zone. Within individual groups, the specific catalytic activity increased with increase in atomic number.

Relationships of this sort are of definite interest for the selection of catalysts, and they are bound to cover various classes of chemical compounds (oxides, sulfides, nitrides, etc.). Great possibilities are opened by the investigation of alloys, the use of which permits finer control over electron structure.

Secondly, we must try to discover the laws of the formation of intermediate surface compounds between the reacting substances and the catalyst and must study the properties of these compounds. In Borekov's opinion, much may be attained in this direction by the use of labeled atoms, since they enable the reactivity of the surface compound to be determined without affecting the composition of the catalyst under investigation.

The third direction of work is concerned with the selection of catalysts for complex reactions occurring in presence of multicomponent catalysts. In this case individual stages may be effected on different parts of the catalyst, and the way in which these are combined in the catalyst and the ratios of their surfaces may affect the selectivity of the process within wide limits.

Apart from these questions — continued G. K. Borekov — we must pay great attention to matters relating to the creation of a definite internal surface and porous structure within the catalyst. There can be no doubt that adequate development of the theories underlying the search for and the selection of catalysts can be brought about only by approaching the problem from every side and examining it from different points of view. It is quite right, therefore, that in the attack on this problem we should bring to bear the efforts of a wide circle of investigators who are themselves developing various theoretical concepts in the field of catalysis. However, the unification of the efforts of various schools of thought must proceed not with an accompanying happy coexistence of various theories, but to the accompaniment of a conflict of opinions. Only in this way can a sound general theory be created and our task completed.

V. V. Voevodsky, Doc. Chem. Sci. (Institute of Chemical Physics of the USSR Academy of Sciences), discussed investigations directed to the development of the chain theory of heterogeneous catalysis. The basis of this theory is the assumption that in most cases rapid surface reactions are brought about by the aid of geometrically localized active intermediate compounds, the fundamental property of which is their ability to react very quickly with low activation energy with molecules of the original substances.

The concept of the existence of free radicals on the surface of heterogeneous catalysts cannot be regarded as original, it has existed in the literature for several decades. The new feature in the theory developed by V. V. Voevodsky was the assumption of the possibility of the formation of surface chains, i.e. the possibility of a process in which, as a result of the indestructibility of the free valency in the reaction of a radical with a molecule, each act of reaction leads to the regeneration of the free radical, so that after the first act, in which a free radical is produced, a large number of further acts may be brought about, resulting in a chain of elementary acts and its propagation.



The application of chain concepts in heterogeneous catalysis is of interest, in Voevodsky's opinion, mainly because it opens up wide possibilities for the use of the theoretical ideas and methods of investigation created and developed in the course of the evolution of the chain theory of homogeneous reactions, for the study of the mechanisms of heterogeneous processes and for the discovery of methods of controlling these processes.

What inferences can already be drawn concerning the mechanism of catalysis from the general postulates of the chain theory? The most interesting is the conclusion that a catalyst has two functions. If the heterogeneous process has a chain character, then as in any other chain process, in an analysis of its course we must take into account the factors having a substantial effect on the initiation and breaking of chains, on the one hand, and on processes of chain propagation, on the other.

Just as in homogeneous chain reactions, the acts of initiation and breaking of chains determine the concentration of radicals, i.e. the rate of the process, but chain-propagation reactions determine the identity of the products, i.e. the direction of the process.

In heterogeneous catalysis it is, of course, to be expected that the rates of all these elementary stages will depend very greatly on the properties of the catalyst.

Hence, in the chain theory, matters relating to the rate and the direction (selectivity) of the catalytic process are clearly separated from one another, and the possibility arises of controlling the processes in these respects, taken separately. In fact — said V. V. Voevodsky — if we have two catalysts, and on one of these chains are readily initiated but the propagation of the chains goes with great difficulty whereas on the other chain propagation reactions are rapid but initiation occurs with difficulty, then the improvement of the catalytic properties of these two catalysts must be effected by quite different methods. In the first case, additions must be made which will encourage reaction between surface radicals and molecules, and in the second, some way must be found to facilitate the reactions in which radicals are formed; i.e. the dissociation reactions of the original molecules at the surface.

These general postulates must be made to serve as the basis of experimental investigations, in the course of which it is our intention to verify the possibility of applying chain concepts in heterogeneous catalysis.

The main ways in which this theory can be experimentally verified, as proposed in a very general form in papers by N. N. Semenov, F. F. Volkenshtein, and V. V. Voevodsky, can be formed into a plan which falls into three parts:

1. Determination of the structures and properties of the active intermediate compounds, local active centers, or, as they have been called, surface radicals. The solution of this problem lies mainly in the application of modern physical methods of investigation.
2. Determination of the chain length. The experiments must consist in the measurement of the number of molecules of products formed for each originally created surface radical, i.e. in the measurement of a peculiar "catalytic" or "radical" yield. If such experiments lead to an unequivocal result, then the occurrence of chain reactions on solid surfaces can be regarded as proved and the question will arise of the extent to which such processes occur.
3. The performance of large number of detailed investigations into the kinetics of various heterogeneous processes. The results in themselves will not be able to provide unequivocal indications of the mechanism of the process, but, in Voevodsky's opinion, in combination with data obtained by the first two methods they may be extremely valuable for the understanding of the nature of the process and for the development of rational methods of controlling it.

In a short address, Academician A. N. Terenin considered matters relating to the investigation of the molecular structures of catalysts, in particular the use for this purpose of modern methods of infrared spectroscopy, paramagnetic resonance, etc.

Summarizing the discussion on Academician A. A. Balandin's paper, the chairman, Academician M. M. Dubinin, pointed out the necessity of planning future theoretical and experimental investigations on the catalysis problem, and he called for united efforts by the various schools with the object of solving this problem. The Scientific Council on the Catalysis Problem, which has been instituted by the Division of Chemical Sciences of the USSR Academy of Sciences and which includes scientists of the Academy of Sciences, industrial institutes, and higher teaching establishments, was called upon to play a dominant part in this matter and to bring about the very necessary coordination of all the investigations being carried out in this field.



Various aspects of the interesting work reported in a paper by Corr. Memb. Acad. Sci. USSR A. D. Petrov at the general meeting of the Division were discussed by Corr. Memb. Acad. Sci. USSR A. P. Terentyev, Prof. P. G. Sergeev, Academician M. M. Dubinin, Prof. K. I. Ivanov, and others.

The paper by Corr. Memb. Acad. Sci. USSR A. P. Terentyev was discussed by Prof. P. G. Sergeev, Acad. I. L. Knunyants, Corr. Memb. Acad. Sci. USSR D. N. Kursanov, and others. In concluding the discussion, Academician M. M. Dubinin pointed out the value of the new system of nomenclature worked out by Corr. Memb. A. P. Terentyev and his coworkers, and he stated that in its relation to the coming discussion of problems of chemical nomenclature at the Fourteenth Congress of the International Union of Pure and Applied Chemistry in Zurich the work carried out in this direction in the Soviet Union would acquire even greater significance.



